

Supplementary Information for

Designing 2D Carbon Dot Nanoreactors for Alcohol Oxidation Coupled with Hydrogen Evolution

Qitao Chen¹, Baodong Mao^{1*}, Yanhong Liu^{1*}, Yunjie Zhou², Hui Huang², Song Wang,³

Longhua Li^{1*}, Wei-Cheng Yan^{1*}, Weidong Shi^{1*} and Zhenhui Kang^{2,4*}

¹School of Chemistry and Chemical Engineering, Jiangsu University, 301 Xuefu Road Zhenjiang 212013, China.

²Institute of Functional Nano and Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-based Functional Materials and Devices, Soochow University, 199 Ren'ai Road, Suzhou 215123, China.

³Hubei Key Laboratory of Low Dimensional Optoelectronic Materials and Devices, Hubei University of Arts and Science, Xiangyang, 441053, China

⁴Macao Institute of Materials Science and Engineering (MIMSE), MUST-SUDA Joint Research Center for Advanced Functional Materials, Macau University of Science and Technology, Taipa 999078, Macao, China.

Corresponding authors:

B. Mao (maobd@ujs.edu.cn); Y. Liu (liuyh@ujs.edu.cn); L. Li (longhuali@ujs.edu.cn)

W. Yan (yanwc@ujs.edu.cn); W Shi (swd1978@ujs.edu.cn); Z. Kang (zhkang@suda.edu.cn)

1. Supporting Texts

1. Experimental section

1.1 Synthesis of catalysts

Synthesis of 0D Cu-ZIS quantum dots (QDs). The Cu-ZIS QDs were synthesized through a previously reported hydrothermal method with modifications¹. First, 0.136 g of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, 0.649 g of $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ and 0.186 g of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (serving as the metal precursors) were dissolved in 8 mL of deionized water containing 0.363 g of L-cysteine (as protective agent). After ultra-sonication for 15 min, 1.0 M NaOH solution was used to adjust the pH of the mixture to 8.5. After stirring for 20 min, the solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave and maintained at 110 °C for 4 h. The samples were collected by centrifugation after adding ethanol, washed three times with deionized water/ethanol, and then dispersed in deionized water for further use.

Synthesis of 1D Cu-ZIS nanowires. In a typical synthesis of Cu-ZIS nanowires with modifications², $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (0.25 mmol) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.05 mmol), $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (0.50 mmol), and TAA (2.00 mmol) were loaded into a 25 mL Teflon-lined autoclave, which was then filled with 12 mL of pyridine. Then 0.65 g of CTAB was added slowly with stirring. After 1 h of magnetic stirring, the autoclave was sealed and maintained at 160 °C for 16 h and then allowed to cool down to room temperature naturally. The pink product was collected by centrifugation, washed several times with absolute ethanol and ioned water, and finally dried under a vacuum at 60 °C for 4 h.

Synthesis of carbon dots (original C-Dots). The original C-Dots were prepared based

on a reported hydrothermal method with some modifications³. Citric acid (1.05 g) and ethylenediamine (335 μ L) were dissolved in deionized water (10 mL), which was then transferred to a 20 mL Teflon-lined autoclave and heated to 180 °C and kept for 5 h. After reaction, the autoclave was cooled down to room temperature naturally. The obtained suspension was then filtered through a 0.22 μ m filter membrane to remove large particles. Transparent the brown-black filtrate was then subjected to dialysis (MWCO: 200 Da) for 3 days to obtain the original C-Dots and then dispersed in deionized water for further use.

1.2 Structure and morphology characterizations

X-ray diffraction (XRD) was used to analyze the samples ranging from 10 to 80° (scan rate: 7.0°/min) with Cu K α radiation source (λ = 1.5417 Å) on a D/MAX-2500 diffractometer (Empyrean, Holland Panalytical). Raman spectroscopy with a scan range of 100–3000 cm⁻¹ was measured using an America DXR Raman spectrometer. An FEI-Tecnai F20 electron microscope was used for transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) with an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a K-Alpha plus XPS system (Thermo Fisher Scientific, USA). A Bruker MultiMode 8 atomic force microscope (AFM) was employed to measure the thickness, and the surface potentials of samples were detected under Kelvin probe force microscopy (KPFM) mode. The X-ray absorption near-edge spectroscopy (XANES) experiments were conducted at Hefei Synchrotron Radiation Facility (NSRL, Beamlines MCD-A and MCD-B (Soochow Beamline for Energy Materials)). All XANES spectra were recorded in the total

electron yield (TEY) mode using a sample current measurement. The XANES raw data were normalized by a procedure consisting of several steps. First, the spectrum recorded for the sample was normalized to the photon flux by division through a spectrum obtained for a freshly sputtered gold wafer, and then substrate a line to set the pre-edge to be zero. Finally, the spectra were normalized to yield an edge-jump to one. The photothermal effect was tested by an all glass automatic on-line trace gas analysis system (Labsolar-6A, Beijing Perfectlight).

1.3 Optical characterizations

UV-vis absorption spectroscopy was characterized with a Cary 8454 spectrometer. A Cary Eclipse fluorescence spectrophotometer was used for photoluminescence (PL) of the samples. Time-resolved PL spectra were collected by excitation at 481 nm using a QuantaMaster TM 40 spectrometer (Photon Technology International, Inc.). For femtosecond (fs) transient absorption spectroscopy (TAS) measurements, the fundamental beam from the Yb:KGW laser (Pharos, Light Conversion Ltd.) was split into several paths and sent to an ultrafast spectrometer (TA100, Time-Tech Spectra, LLC). One light path was introduced into a noncollinear optical parametric amplifier to generate a pump pulse at a certain wavelength. Meanwhile, another path was focused onto a YAG crystal to produce a continuum light as the probing beam. Both pump and probing light beams spatially overlapped at the sample, and the time delay between the two lights was controlled using the motorized positioning system. In detail, the femtosecond laser of 320 nm was adopted as the pump light and the wide broadband femtosecond light from 350–700 nm was adopted as the probe light. Ultraviolet

Photoelectron Spectroscopy (UPS, Thermo ESCALAB 250XI) was used to determine the work function of samples.

1.4 Photoelectrochemical measurements

Electrochemical impedance spectra (EIS) and photocurrent response were measured on a CHI 760E electrochemical workstation (Chenhua, China) with a standard three-electrode cell and 0.5 M Na₂SO₄ solution as the electrolyte with the samples uniformly distributed on fluoroalkane doped tin oxide (FTO) glass. In a typical process, 10 mg of the as-obtained catalyst was dispersed in a solution containing 1 ml of ethanol, 5 mg of polyvinyl pyrrolidone, and 0.02 mL of oleic acid, which was ultrasonically treated for 30 minutes. Then, the solution was gradually applied to a clean 1 × 2 cm² FTO glass electrode using a spin coater. The photocurrent was measured under illumination of a 300 W xenon lamp. The electrocatalytic hydrogen evolution reaction properties of all samples were tested in a typical three-electrode system using CHI 760E (Chenhua, Shanghai China) with the ZIS, Cu-ZIS and Cu-ZIS/C-Dots on FTO as the working electrodes, a graphite rod as the counter electrode, and a Ag/AgCl electrode as the reference electrode, respectively.

1.5 The calculation of HOMO and LUMO levels

The measurement of cyclic voltammetry (CV) curve of C-Dots was carried out in an acetonitrile solution containing tetrabutylamine hexafluorophosphate (TBAP) saturated with nitrogen, using ferrocene as the standard, and glassy carbon electrode, Ag/Ag⁺ electrode and carbon rod as the working, reference and counter electrodes, respectively.

The calculation formula is as follows⁴⁻⁹:

$$E_{HOMO} = -(E_{onset}^{ox} - E_{ferrocene} + 4.8) \text{ eV} \quad (1)$$

$$E_{LUMO} = -(E_{onset}^{red} - E_{ferrocene} + 4.8) \text{ eV} \quad (2)$$

$$E(\text{RHE}, \text{pH} = 7) = E(\text{RHE}, \text{pH} = 0) - 0.059 \text{ pH V} \quad (3)$$

$$E_F(\text{RHE}, \text{pH} = 0) = 4.5 \text{ V} - E_F \text{ (vs vacuum level) V} \quad (4)$$

1.6 DFT calculations

The density functional theory (DFT) calculations were carried out by using the Vienna Ab-initio Simulation Package (VASP)¹⁰. The electron exchange-correlation interaction was treated by the generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) function¹¹. The interaction between ion cores and valence electrons was described through the method of projection enhanced plane wave (PAW)¹². The kinetic energy cutoff of the plane-wave basis is 500 eV and the energy convergence level is 10^{-5} eV. During structural optimization, the force on each atom was converged to 0.02 eV/Å and the top stoichiometric layer was allowed to relax, while the bottom stoichiometric layer was fixed in its main body position. To eliminate the periodic interaction, the size of the vacuum space was set to 15 Å along the z direction. The Gibbs free energy was defined as follows¹³:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \quad (5)$$

where ΔE (DFT), ΔZPE , T and ΔS are the DFT calculated total energy, zero-point energy (ZPE), temperature (300 K here by assume) and entropy, respectively. The adsorption energy (E_{ad}) of the adsorbed species was computed using the formula $E_{ad} = E_{ads} + E_{sub} - E_{tot}$, where E_{tot} refers to the total energy of the system comprising both the substrate and adsorbate, and E_{sub} and E_{ads} denote the ground energy of the substrate and

the adsorbate, respectively. According to this definition, the strength of adsorption increases as the adsorption energy becomes more positive.

The surface energy was developed by Reuter and Scheffler¹⁴. For the surface system the surface free energy $\gamma(T, P)$ in an oxygen pressure P and temperature T is defined as^{15,16}:

$$\gamma = \frac{1}{2A} (G_{\text{Cu-ZnIn}_2\text{S}_4}^{\text{slab}}(T, P) - N_{\text{Cu}}\mu_{\text{Cu}}(T, P) - N_{\text{S}}\mu_{\text{S}}(T, P) - N_{\text{Zn}}\mu_{\text{Zn}}(T, P) - N_{\text{In}}\mu_{\text{In}}(T, P)) \quad (6)$$

where $G_{\text{Cu-ZnIn}_2\text{S}_4}^{\text{slab}}$ is the Gibbs free energy of the slab system; $\mu_{\text{Cu}}(T, P)$, $N_{\text{S}}\mu_{\text{S}}(T, P)$, $N_{\text{Zn}}\mu_{\text{Zn}}(T, P)$ and $N_{\text{In}}\mu_{\text{In}}(T, P)$ are the chemical potentials of Cu, S, Zn and In atoms, respectively; A is the area of the surface unit cell; N_{Cu} , N_{S} , N_{Zn} and N_{In} are the numbers of Cu, S, Zn and In atoms in the slab. Because the surface system is modeled by a slab with two equivalent surfaces, the surface free energy is multiplied by a factor of 0.5.

1.7 COMSOL Simulation Procedure

The numerical simulation is calculated at steady state of Poisson-Nernst Planck equations. The transport of solvated ionic species and charge transfer are considered.

The equations govern the diffusion and electric migration of ionic species are as follows:

$$\mathbf{J}_i = -D_i(\nabla c_i + \frac{c_i n_i F}{RT} \nabla \varphi) \quad (7)$$

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{J}_i = 0 \quad (8)$$

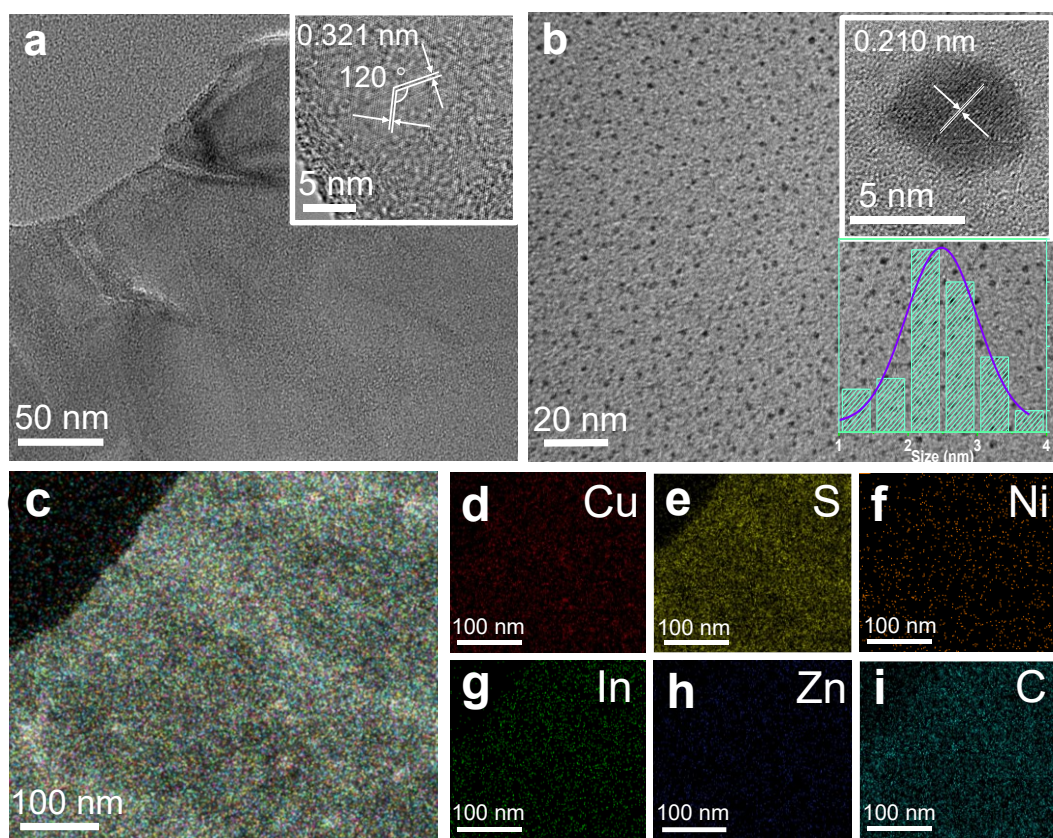
$$\mathbf{E} = -\nabla \varphi \quad (9)$$

$$\nabla \cdot (\varepsilon_0 \varepsilon_r \mathbf{E}) = \rho_v \quad (10)$$

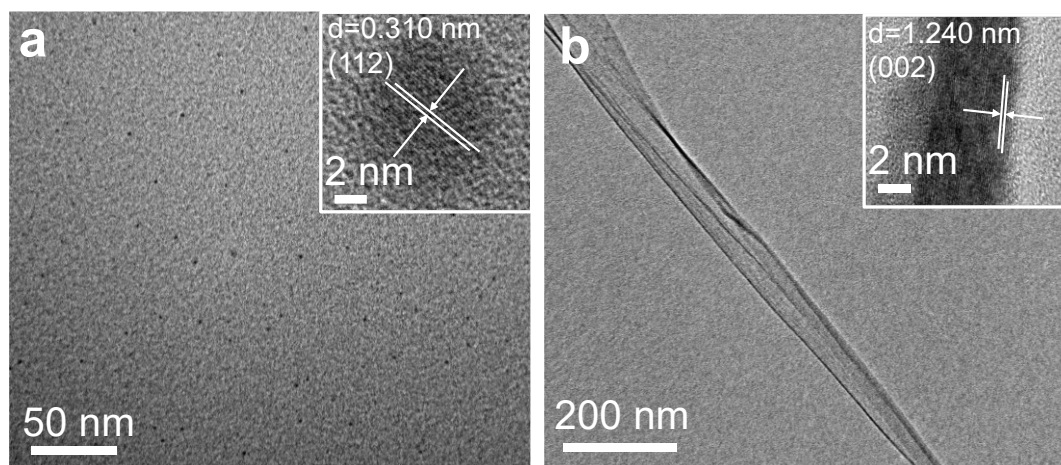
where c_i is noted for the concentration of species i (with $i = \text{H}^+$), D_i is the diffusion coefficient of species i , n_i for the charge of species i . F is the Faraday constant. R and T

are the ideal gas constant and the temperature. φ denotes for the potential and $\mathbf{E}$ denotes for electric field. ε_0 is the dielectric constant in vacuum, ε_r is the relative dielectric constant of the material which consists of a real part and image part. ρ_v is the volume charge density. The electric field was obtained by solving Eqs.(9)-(10). The corresponding COMSOL Simulation parameter values are shown in Supplementary Table 8.

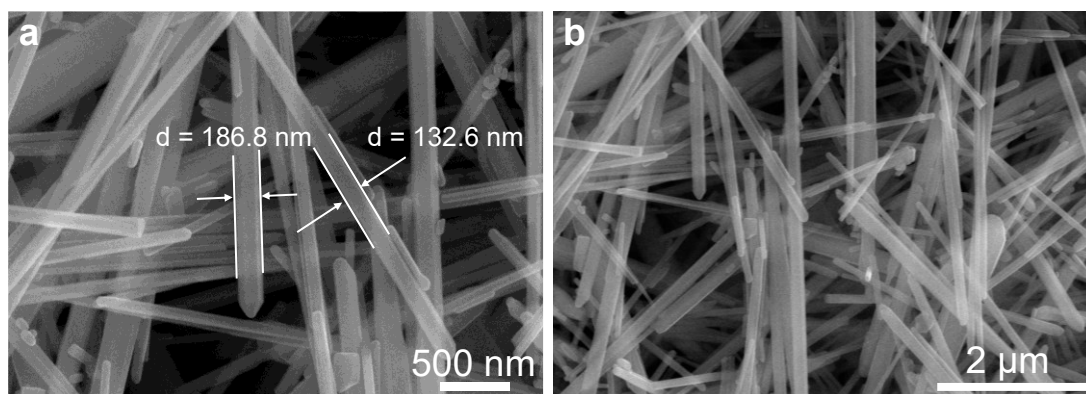
Supplementary Figures



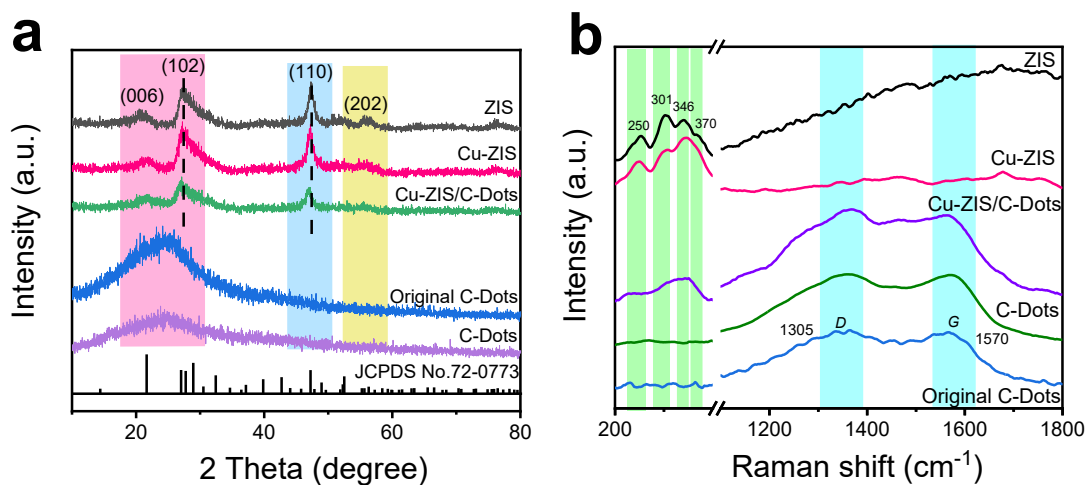
Supplementary Fig. 1. Morphology characterization of Cu-ZIS nanosheets and C-Dots. TEM images of (a) Cu-ZIS nanosheets and (b) C-Dots and the corresponding HRTEM images (top insets) and size distribution histogram (bottom inset in b) obtained by counting 100 particles. (c) EDX overlap and element mapping for (d) Cu, (e) S, (f) Ni, (g) In, (h) Zn, and (i) C profiles of the Cu-ZIS/C-Dots.



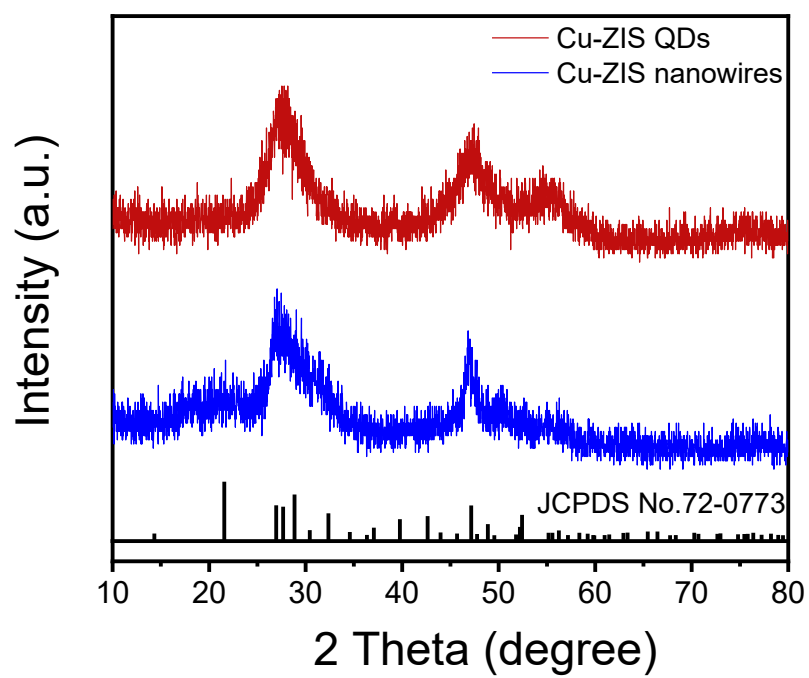
Supplementary Fig. 2. Morphology of 0D QDs and 1D nanowires of Cu-ZIS. TEM images of (a) Cu-ZIS QDs and (b) Cu-ZIS nanowires and the corresponding HRTEM images (insets).



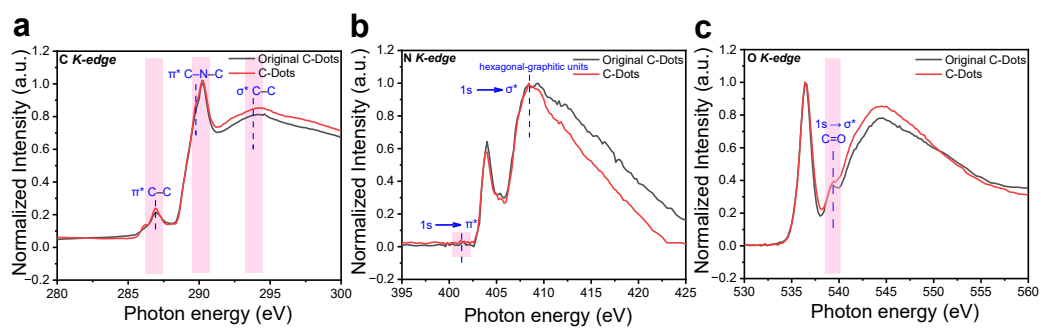
Supplementary Fig. 3. Morphology of 1D nanowires of Cu-ZIS. (a, b) SEM images of Cu-ZIS nanowires at different magnifications.



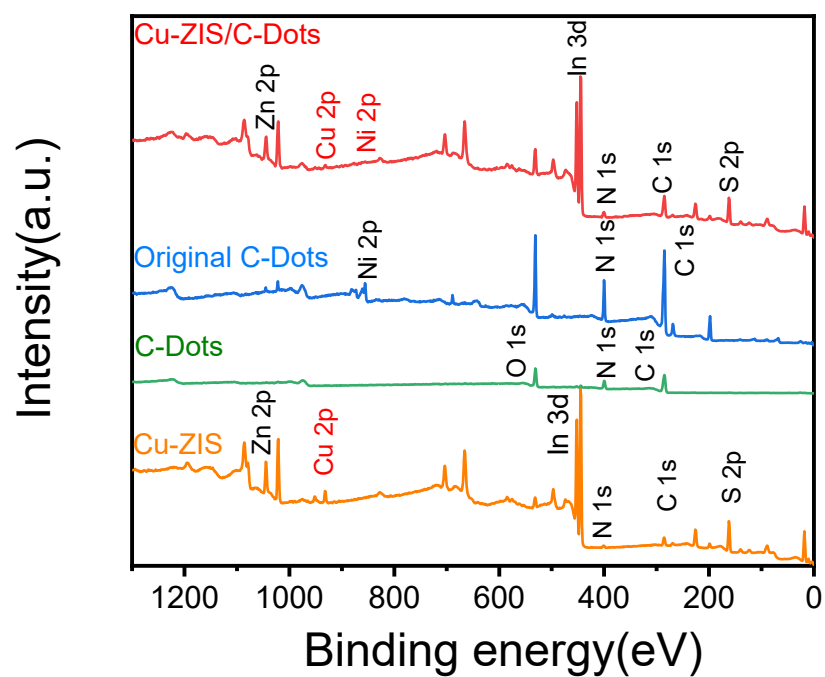
Supplementary Fig. 4. Structure characterizations of the photocatalysts. (a) XRD patterns and (b) Raman spectra of ZIS, Cu-ZIS, original C-Dots, C-Dots and Cu-ZIS/C-Dots. It is observed that the doping of Cu into ZIS reduces the peak intensity with slight red shifts, which is ascribed to smaller ionic radius of Cu(II) than that of Zn(II) leading to the structural deformation of the ZIS lattice^{17,18}. For Cu-ZIS/C-Dots, these four peaks are further reduced and hardly to be observed upon introduction of C-Dots¹⁹.



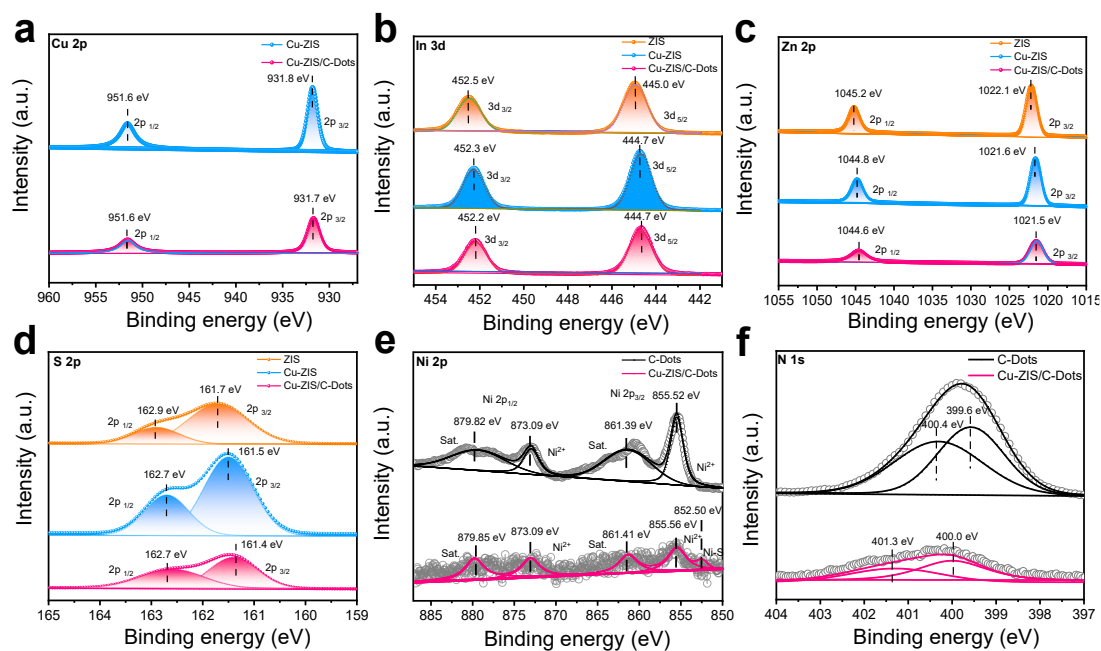
Supplementary Fig. 5. Structural analysis by XRD. XRD patterns of Cu-ZIS QDs and nanowires.



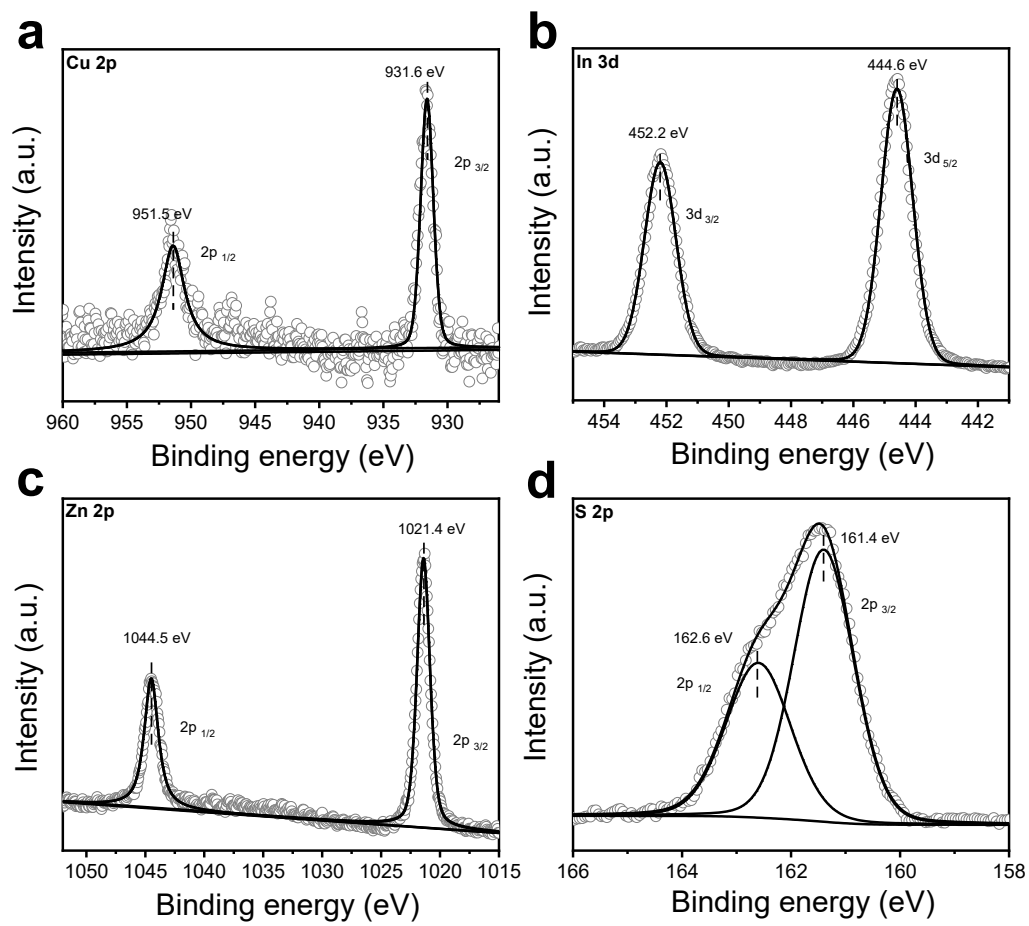
Supplementary Fig. 6. Structural analysis of original C-Dots and C-Dots by XANES. (a) C, (b) N and (c) O K-edge XANES spectra of original C-Dots and C-Dots.



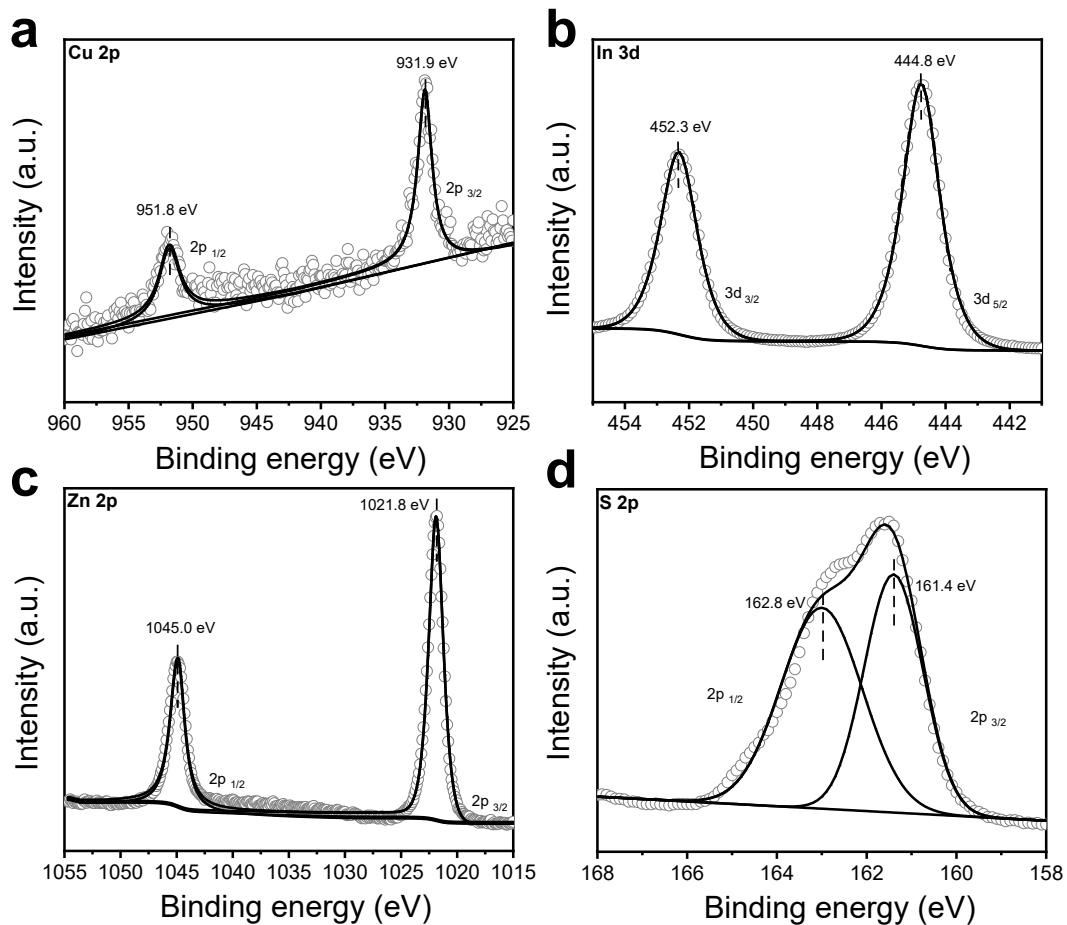
Supplementary Fig. 7. XPS survey spectra. The XPS survey spectra of Cu-ZIS, C-Dots, original C-Dots and Cu-ZIS/C-Dots.



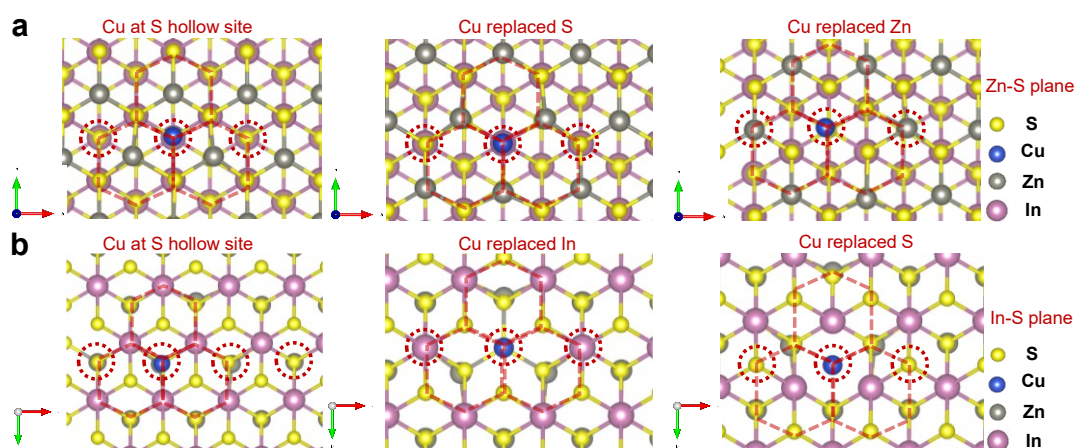
Supplementary Fig. 8. High-resolution XPS analysis of the samples. High-resolution XPS curves: (a) Cu 2p in Cu-ZIS and Cu-ZIS/C-Dots; (b) In 3d, (c) Zn 2p, (d) S 2p in ZIS, Cu-ZIS and Cu-ZIS/C-Dots; (e) Ni 2p and (f) N 1s in C-Dots and Cu-ZIS/C-Dots.



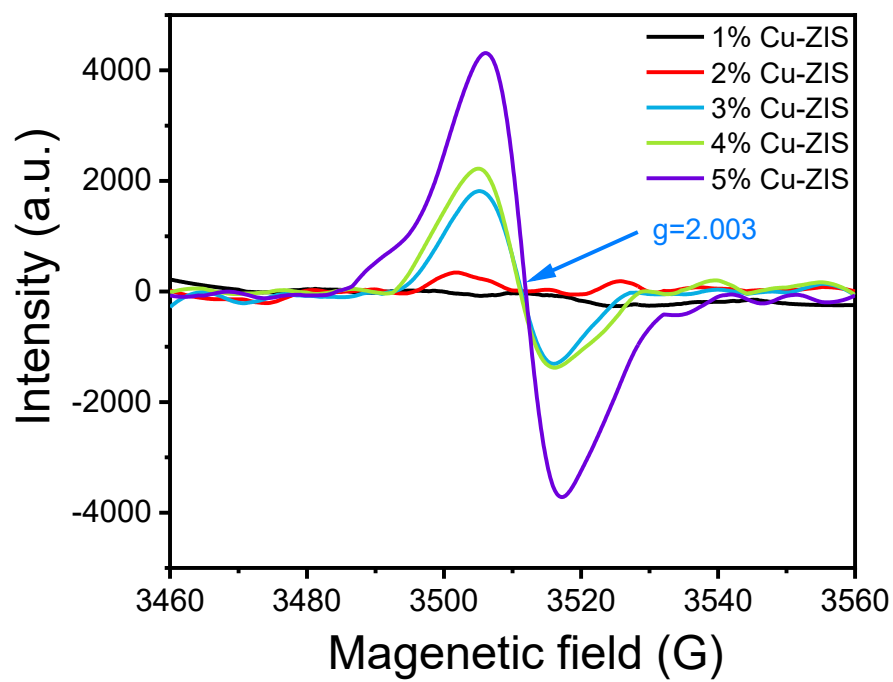
Supplementary Fig. 9. High-resolution XPS analysis of Cu-ZIS QDs. High-resolution XPS curves of (a) Cu 2p, (b) In 3d, (c) Zn 2p and (d) S 2p in Cu-ZIS QDs.



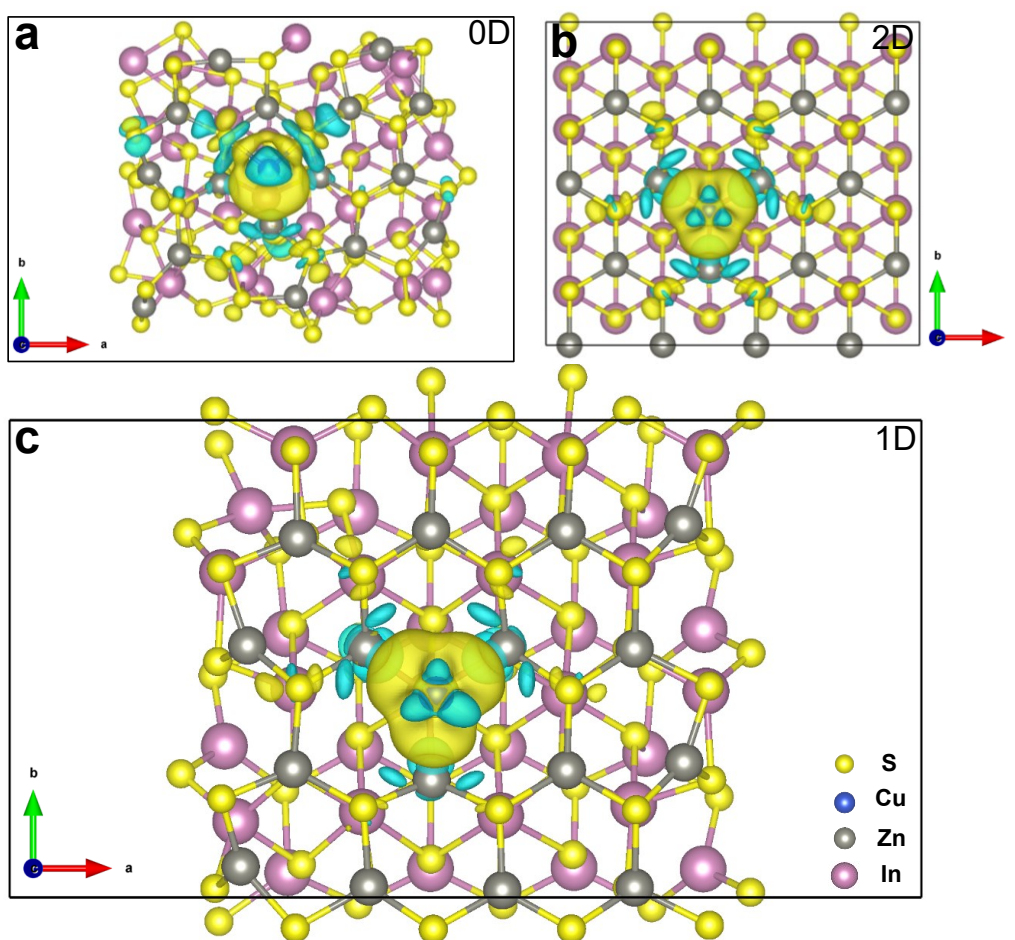
Supplementary Fig. 10. High-resolution XPS analysis of Cu-ZIS nanowires. High-resolution XPS curves of (a) Cu 2p, (b) In 3d, (c) Zn 2p and (d) S 2p in Cu-ZIS nanowires.



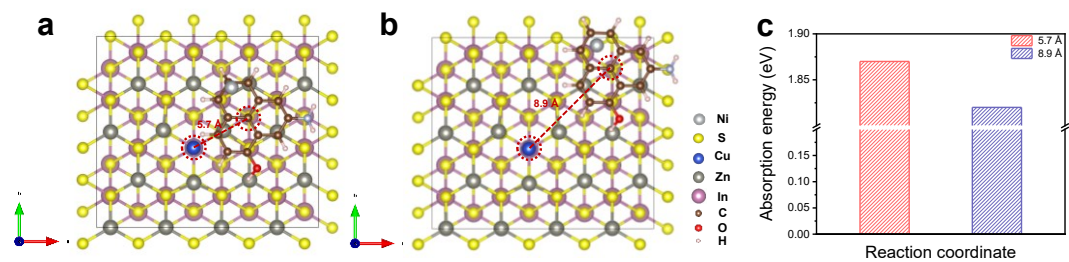
Supplementary Fig. 11. Optimized structure of Cu(II) at various sites for surface energy calculation in Cu-ZIS. Optimized structure of Cu(II) at six different sites for surface energy calculation: (a) three possible sites of Cu(II) in the [Zn–S] layers, and (b) three possible sites of Cu(II) at [In–S] layers. (The yellow, gray, pink, and blue spheres represent the S, Zn, In, and Cu atoms, respectively).



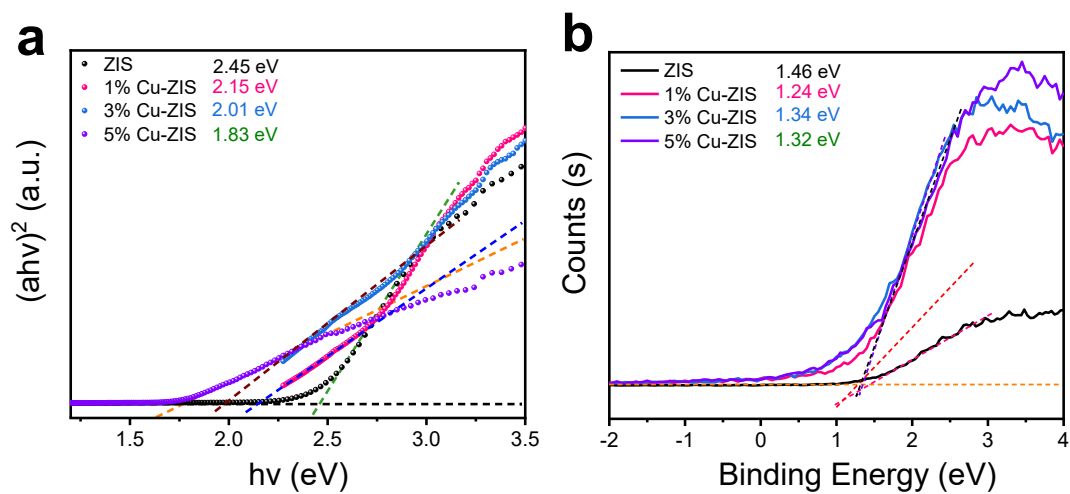
Supplementary Fig. 12. EPR spectra analysis. EPR spectra of x% Cu-ZIS (x = 1–5) for the S vacancy test.



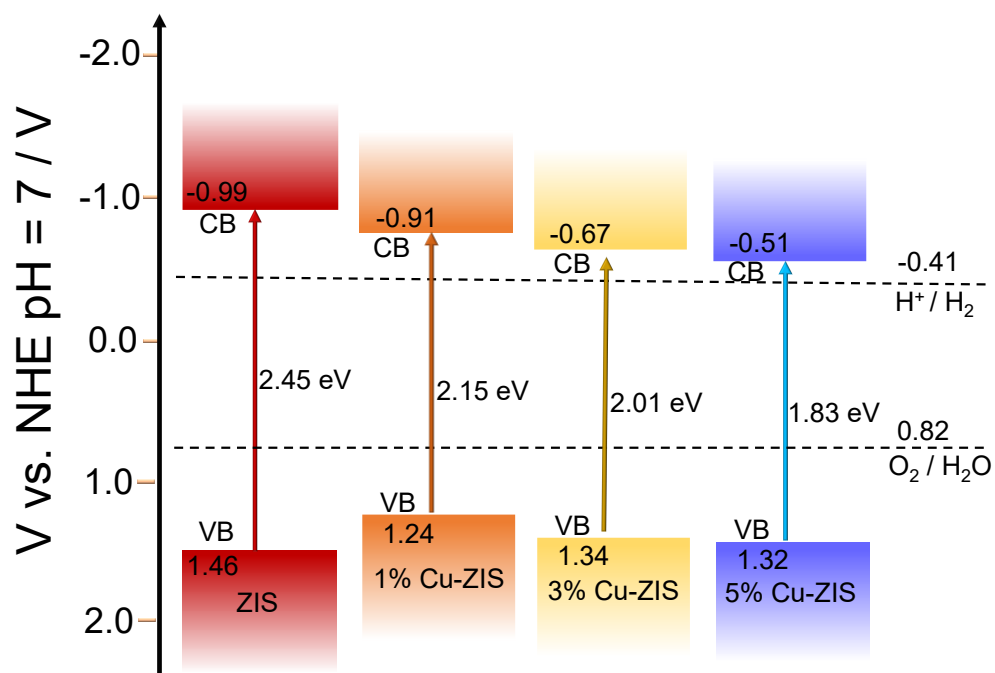
Supplementary Fig. 13. Charge density difference analysis. Top view of charge density difference of (a) Cu-ZIS QDs (0D), (b) Cu-ZIS nanosheets (2D) and (c) Cu-ZIS nanowires (1D) by DFT calculation on the (001) crystal plane.



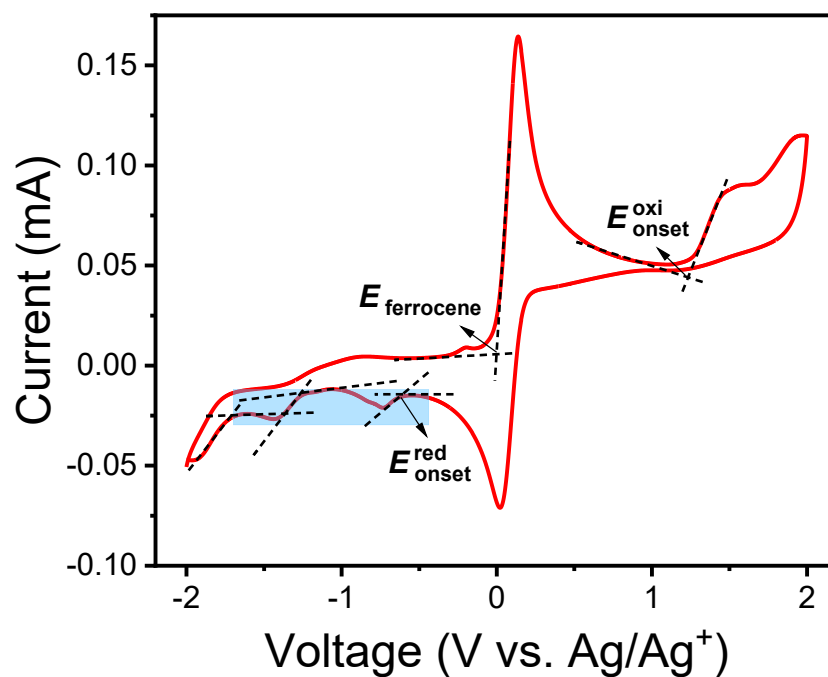
Supplementary Fig. 14. Adsorption of Cu(II) on C-Dots at varying distances. Top view of the C-Dots center and Cu(II) with different distances: (a) 5.7 Å and (b) 8.9 Å. (c) The calculated adsorption energy according to (a) and (b).



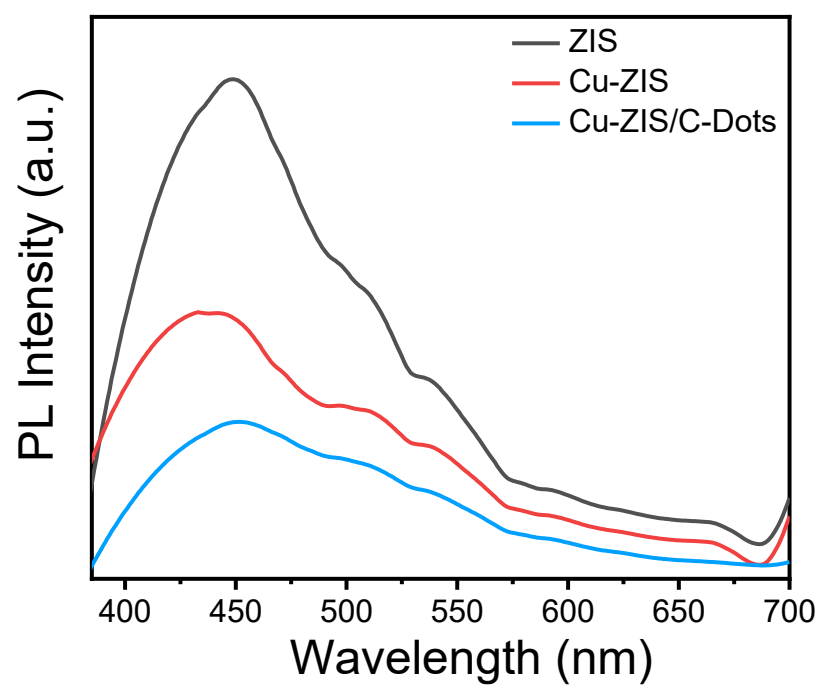
Supplementary Fig. 15. The band level estimation of the photocatalysts. (a) Tauc plots of $(ah\nu)^2$ vs. $h\nu$, and (b) XPS valence band spectra of ZIS and X% Cu-ZIS (X=1, 3, 5).



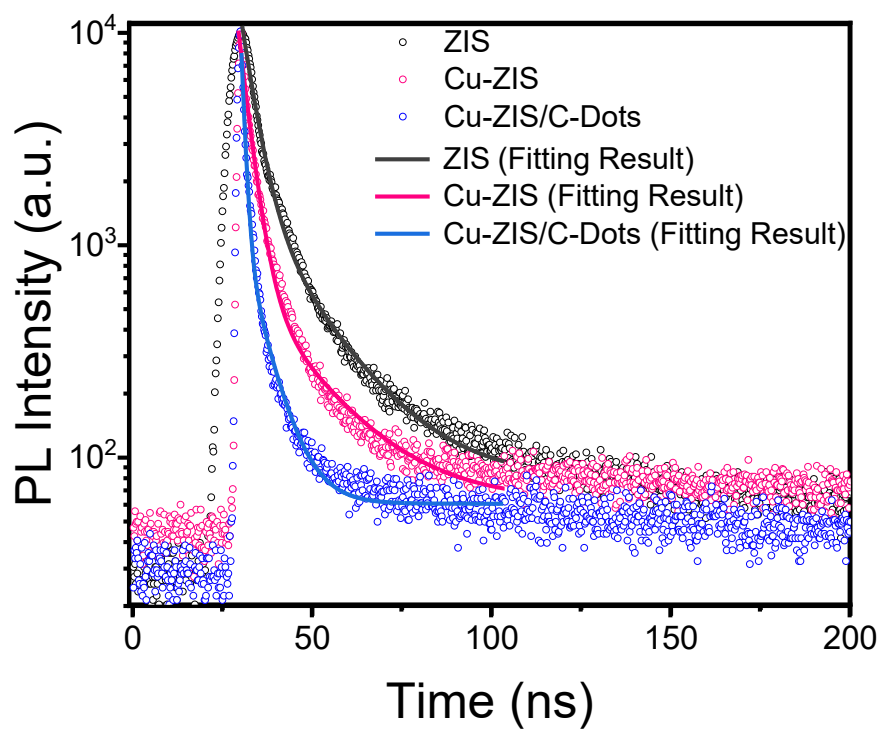
Supplementary Fig. 16. Band alignment. Band structure of ZIS and X% Cu-ZIS (X=1, 3, 5).



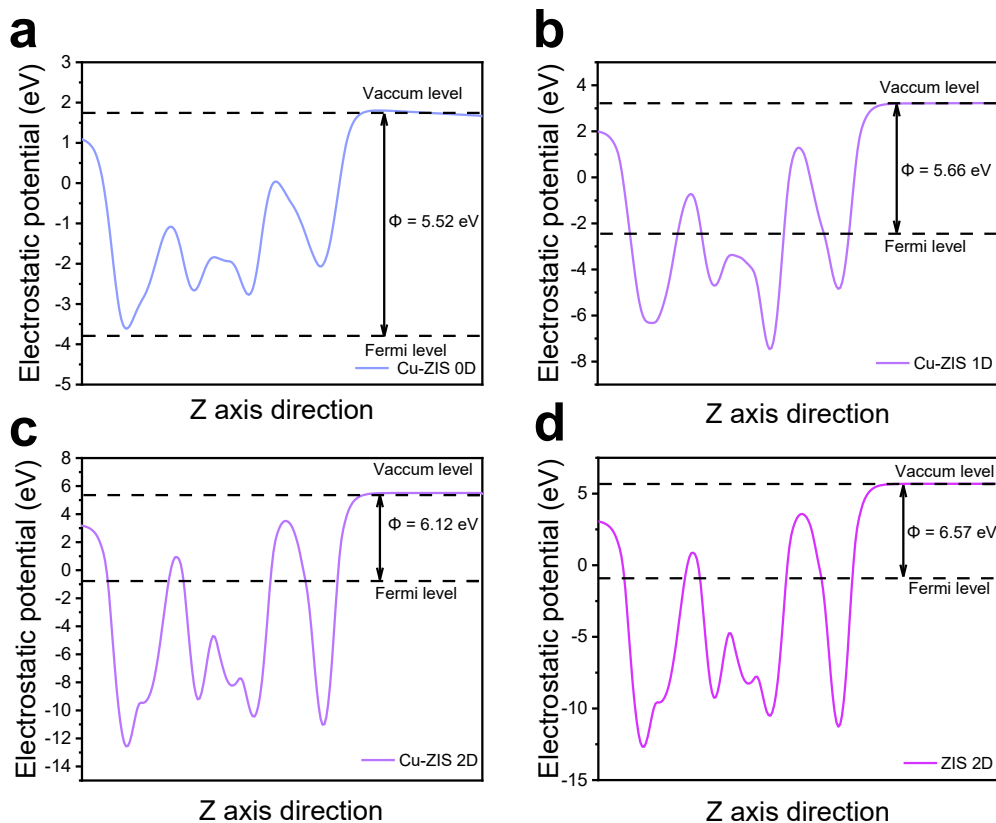
Supplementary Fig. 17. The estimation of HOMO and LUMO levels of C-Dots. CV curve of C-Dots with ferrocene used as the reference material performed in anhydrous acetonitrile.



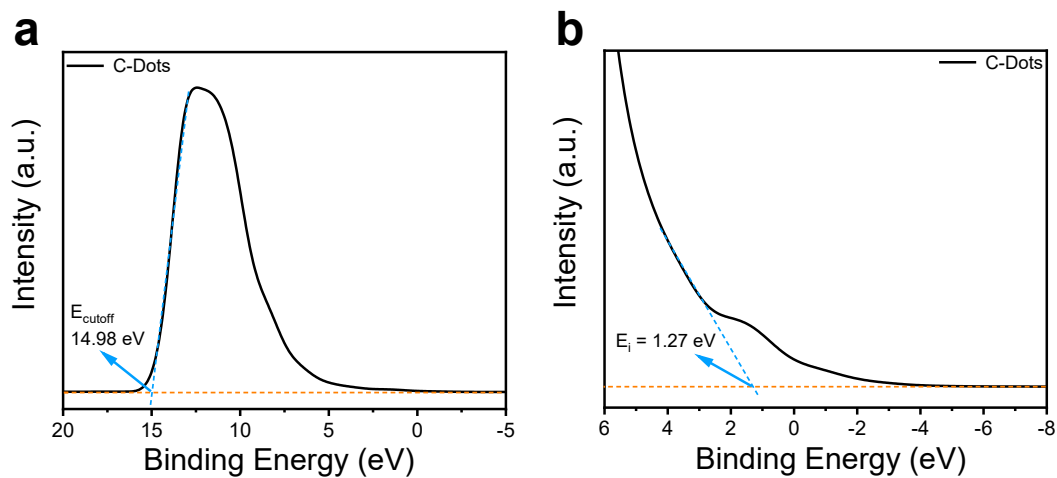
Supplementary Fig. 18. PL spectra. PL spectra of ZIS, Cu-ZIS and Cu-ZIS/C-Dots.



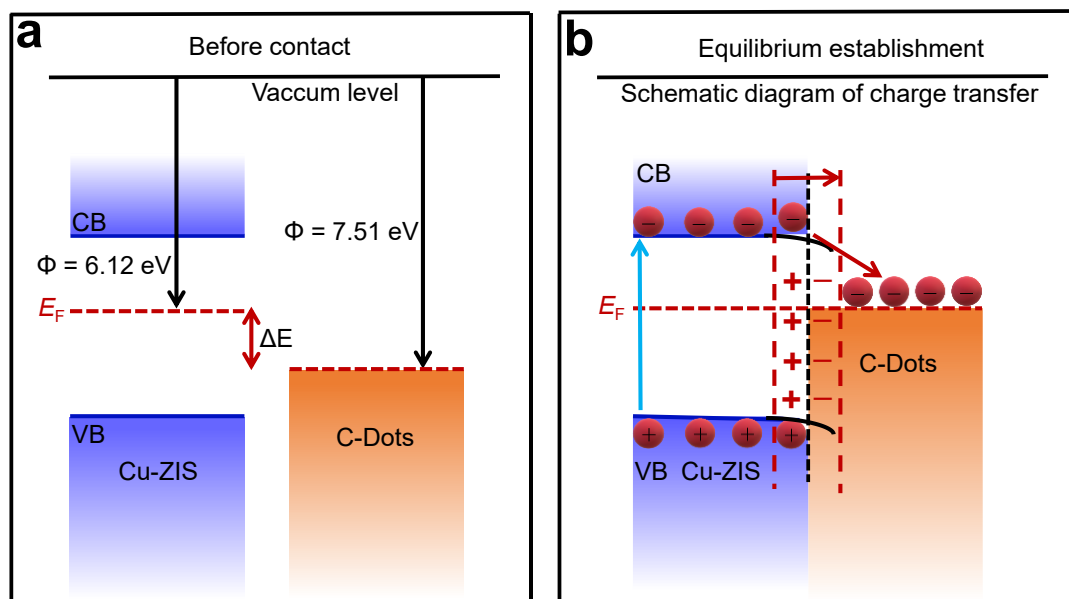
Supplementary Fig. 19. Time-resolved PL spectra analysis. Time-resolved PL spectra of ZIS, Cu-ZIS and Cu-ZIS/C-Dots.



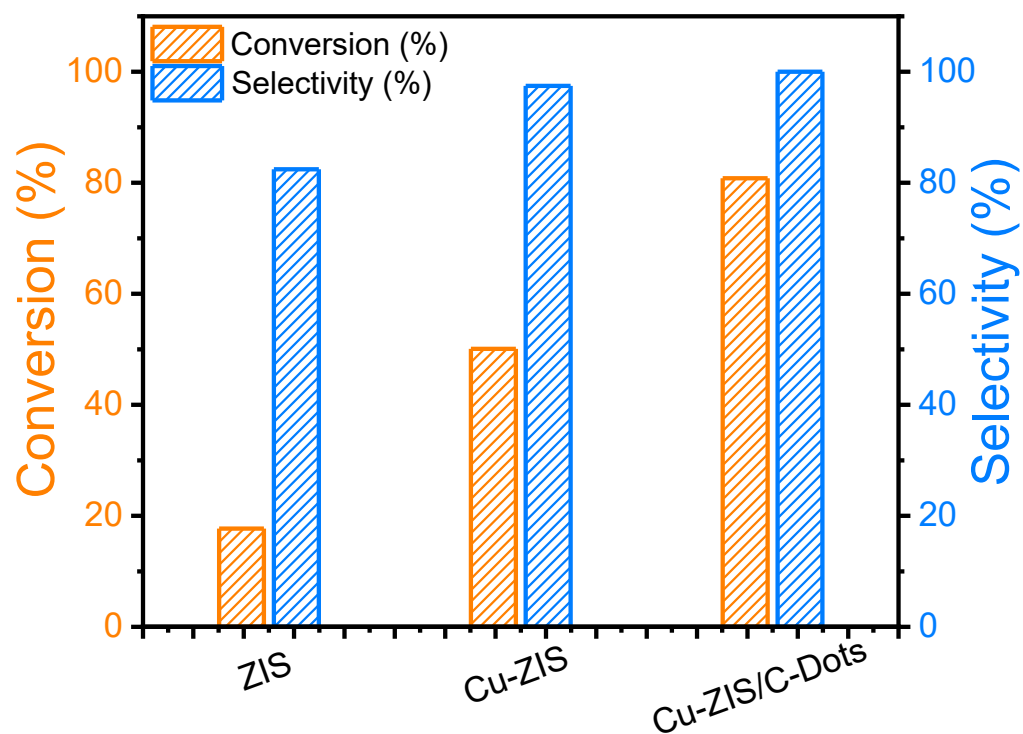
Supplementary Fig. 20. Average potential profiles. Calculated average potential profile along the z-axis of (a) Cu-ZIS QDs, (b) Cu-ZIS nanowires, (c) Cu-ZIS nanosheets and (d) ZIS nanosheets.



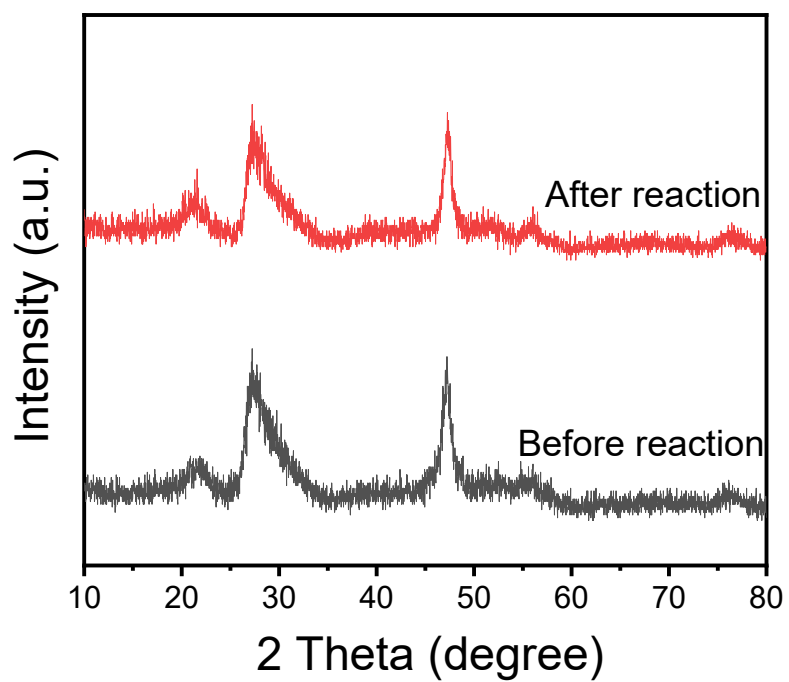
Supplementary Fig. 21. UPS analysis of C-Dots. The UPS spectra in the (a) cutoff (E_{cutoff}) and (b) onset (E_i) energy regions of C-Dots. The ionization energy values (equivalent to the work function (Φ)) of C-Dots ($h\nu = 21.22 \text{ eV}$) were determined by the equation of $\Phi = 21.2 \text{ eV} - (E_{\text{cutoff}} - E_i)$ as 7.51.



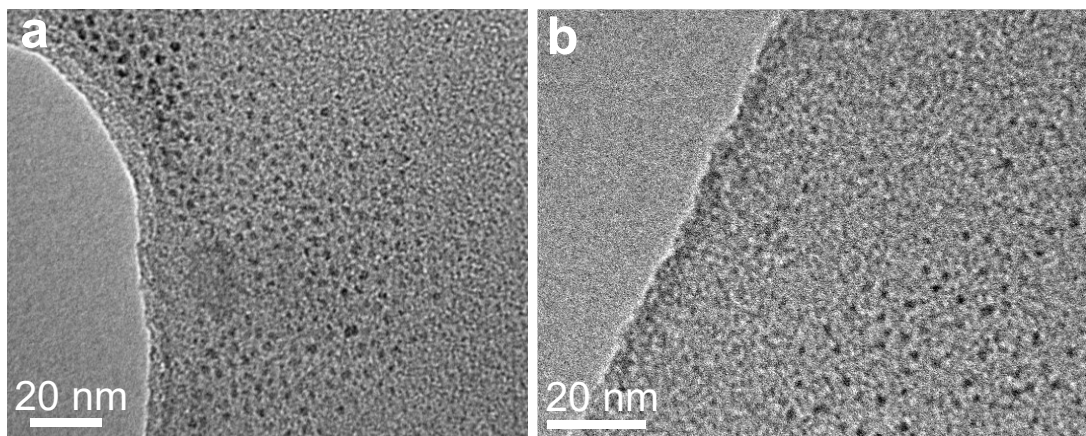
Supplementary Fig. 22. Schematic diagram of charge transfer. Energy level scheme of Cu-ZIS and C-Dots (a) before and (b) after contact for the charge transfer route at the interface of Cu-ZIS/C-Dots.



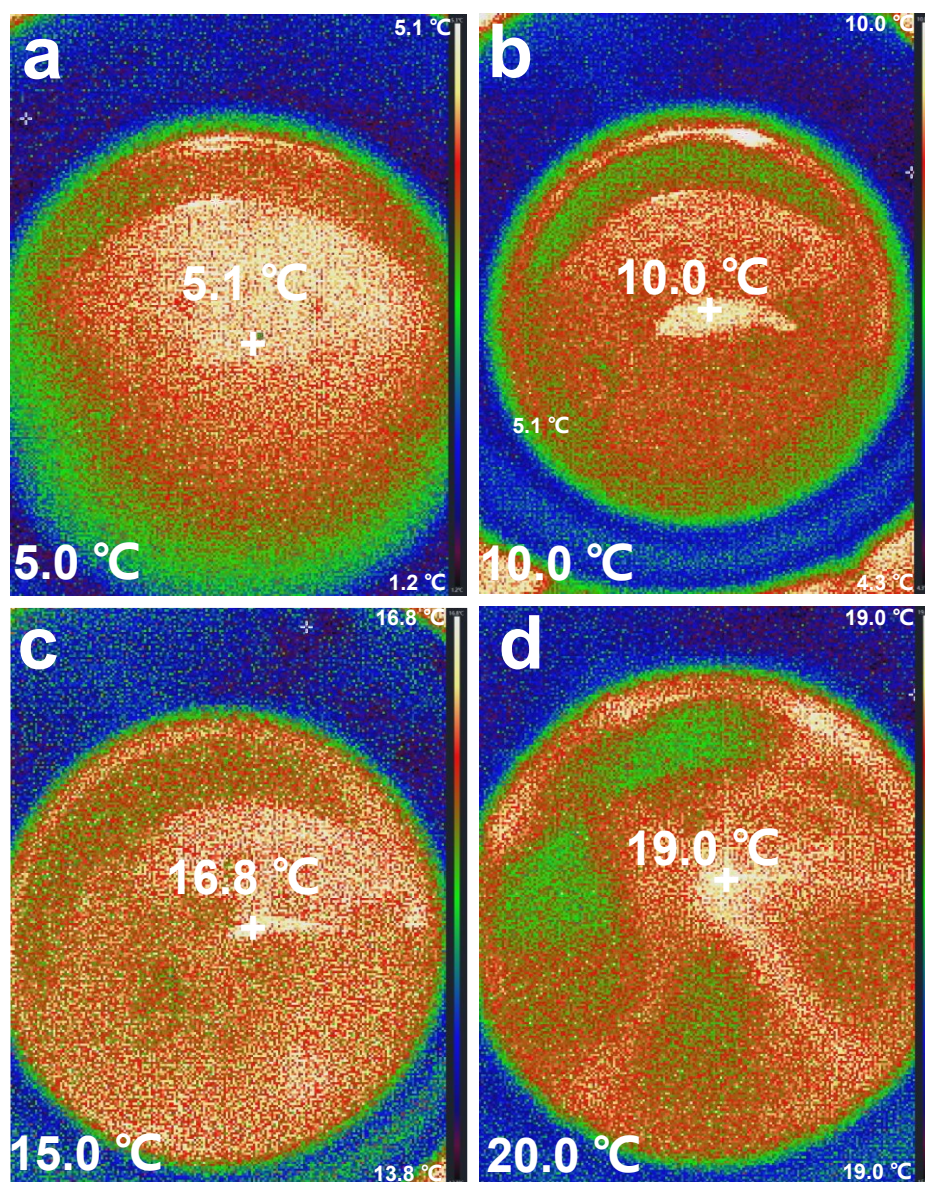
Supplementary Fig. 23. BA conversion and BAD selectivity. The BA conversion and BAD selectivity for ZIS, Cu-ZIS and Cu-ZIS/C-Dots after 5 h of reaction.



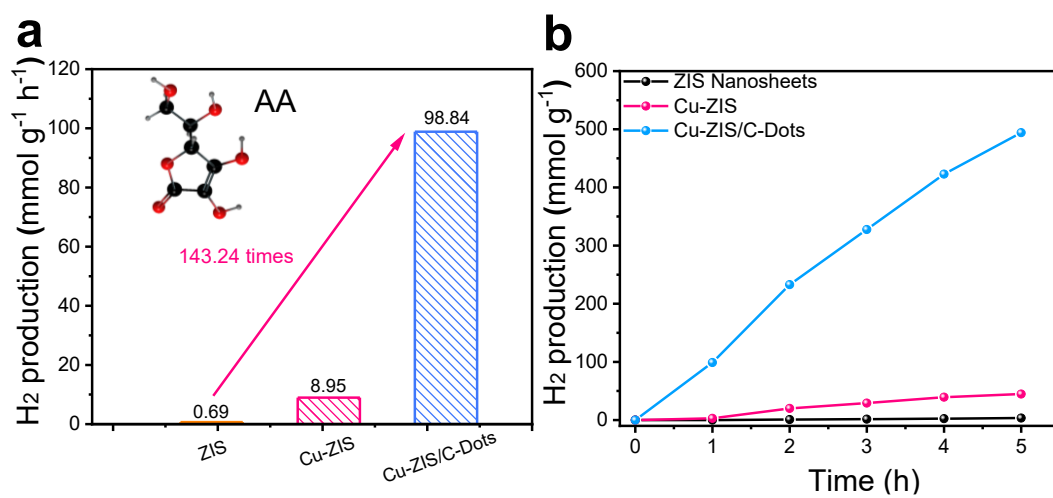
Supplementary Fig. 24. XRD characterization for stability test. XRD patterns of Cu-ZIS/C-Dots before and after photocatalytic hydrogen production.



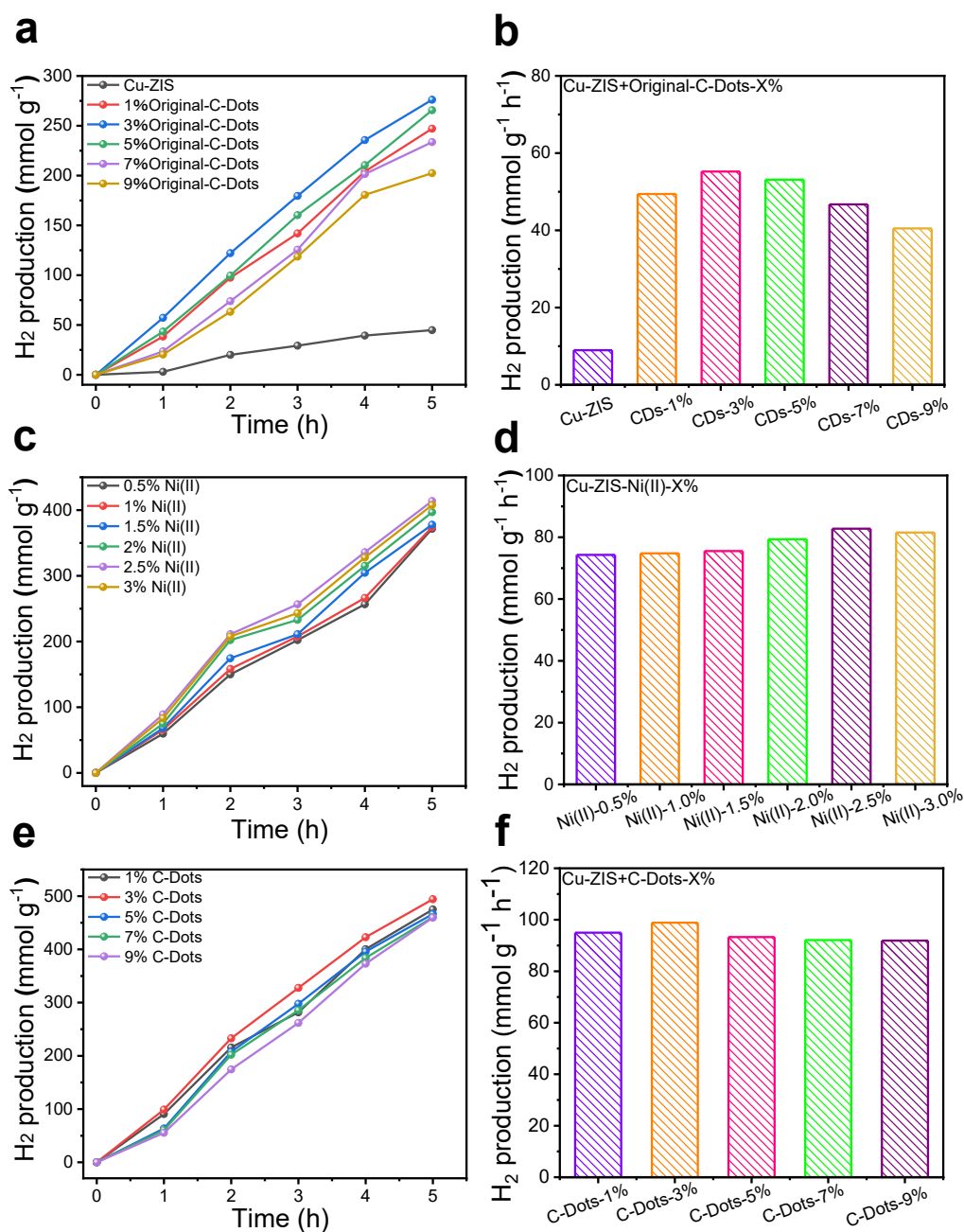
Supplementary Fig. 25. TEM characterization for stability test. TEM images of Cu-ZIS/C-Dots before (a) and after (b) four cycles of photocatalytic hydrogen production.



Supplementary Fig. 26. Characterization of photothermal effect. The infrared photothermal images of Cu-ZIS/C-Dots under different reaction temperatures upon light irradiation with a cutoff filter of $\lambda \geq 420$ nm. The system temperature is controlled at (a) 5.0, (b) 10.0, (c) 15.0 and (d) 20.0 °C, with the actual temperature of 5.1, 10.0, 16.8 and 19.0 °C, respectively.

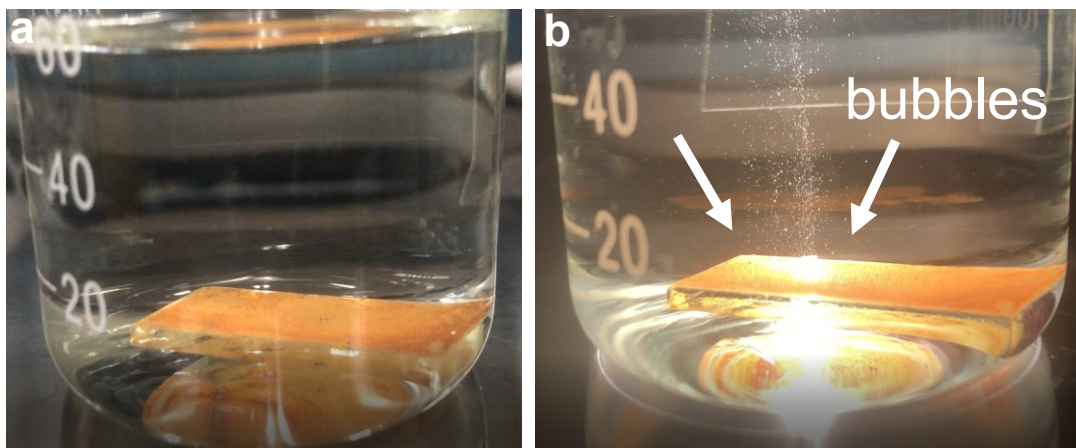


Supplementary Fig. 27. Photocatalytic performance of ZIS, Cu-ZIS and Cu-ZIS/C-Dots with AA. (a) Hydrogen evolution rate and (b) time-dependent hydrogen evolution profile of ZIS, Cu-ZIS and Cu-ZIS/C-Dots photocatalysts with AA as the hole sacrificial reagent.

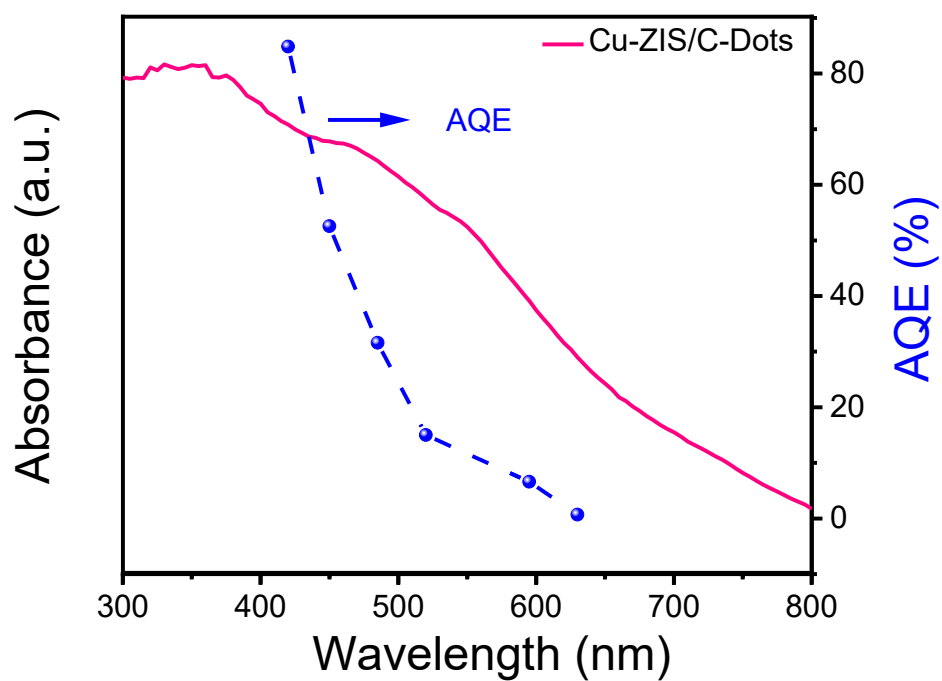


Supplementary Fig. 28. Photocatalytic performance of different catalysts with AA.

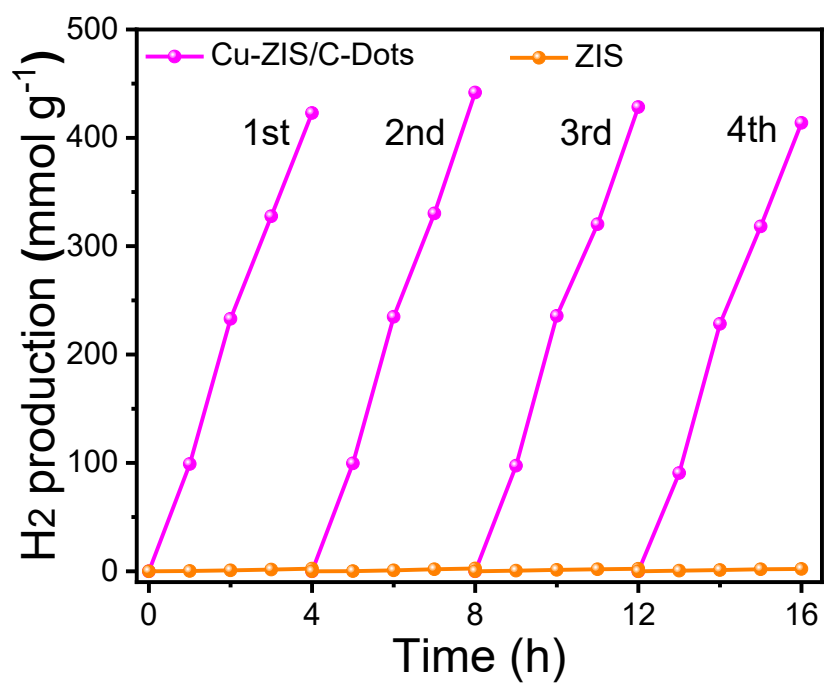
Amount of hydrogen production with (a) Cu-ZIS-X% Original C-Dots, (c) Cu-ZIS-X% Ni(II), and (e) Cu-ZIS-X% C-Dots with AA as the sacrificial agent. The corresponding hydrogen production rate of the samples with (b) Cu-ZIS-X% Original C-Dots, (d) Cu-ZIS-X% Ni(II), and (f) Cu-ZIS-X% C-Dots.



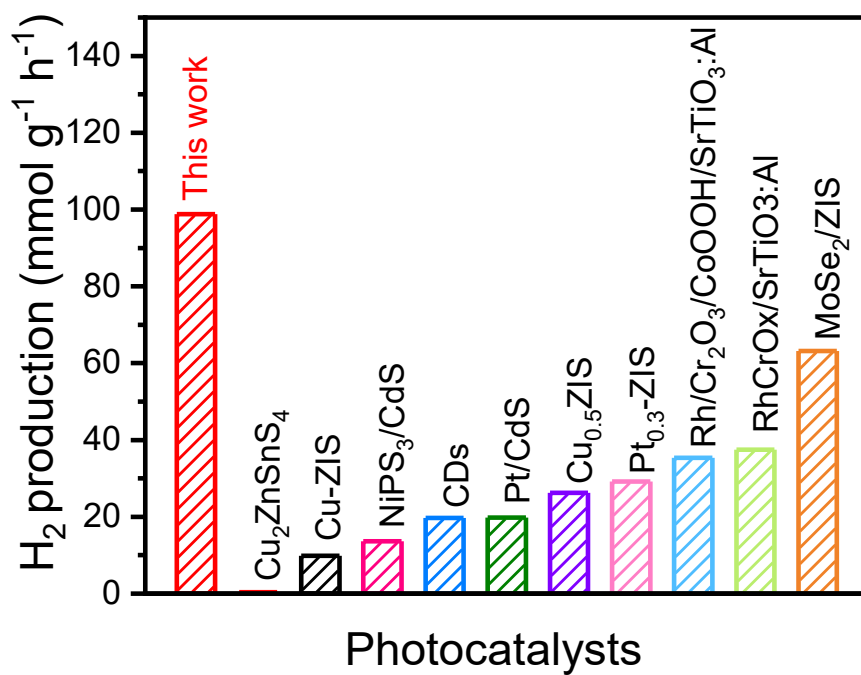
Supplementary Fig. 29. The photographs during photocatalytic reaction. Digital photographs of H_2 evolution using the Cu-ZIS/C-Dots film without (a) and with (b) visible light irradiation.



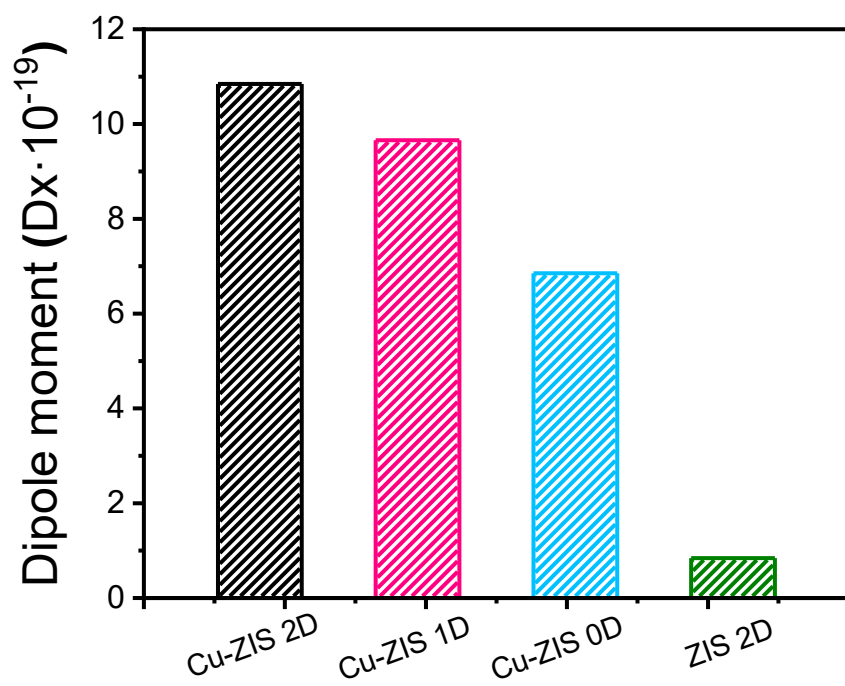
Supplementary Fig. 30. AQE analysis with AA. Wavelength-dependent AQE of H_2 production over Cu-ZIS/C-Dots with AA as the sacrificial reagent in comparison with the absorption spectrum.



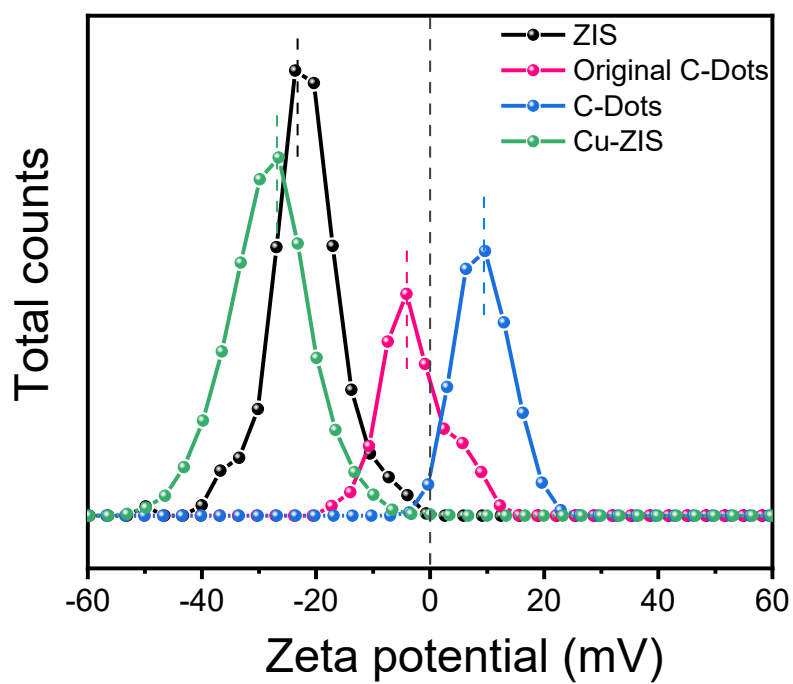
Supplementary Fig. 31. Photocatalytic stability test with AA. Hydrogen production cycle stability of ZIS and Cu-ZIS/C-Dots with AA as the sacrificial reagent.



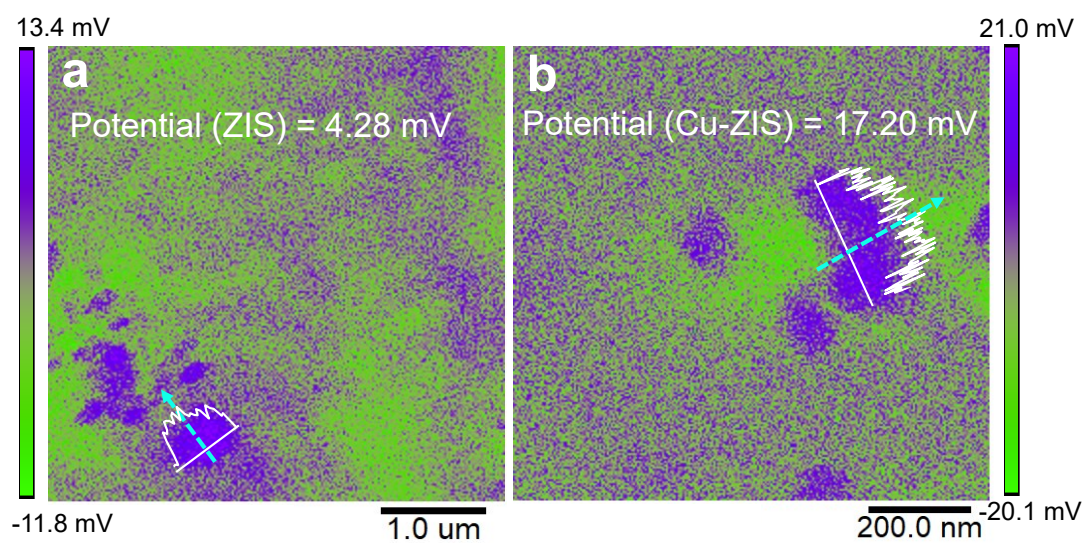
Supplementary Fig. 32. Photocatalytic performance comparison using AA. H₂ production rates for Cu-ZIS/C-Dots with AA as the sacrificial reagent in this work compared with the state-of-the-art photocatalysts.



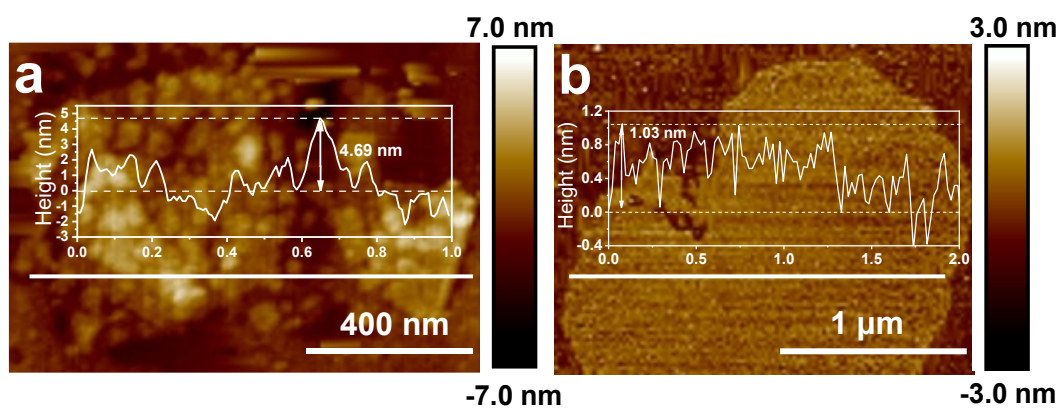
Supplementary Fig. 33. Dipole moment analysis. Dipole moments of 2D Cu-ZIS nanosheets, 1D Cu-ZIS nanowires, 0D Cu-ZIS QDs and 2D ZIS nanosheets.



Supplementary Fig. 34. Zeta potentials analysis. The zeta potentials of ZIS, Original C-Dots, C-Dots and Cu-ZIS dispersed in pure water.

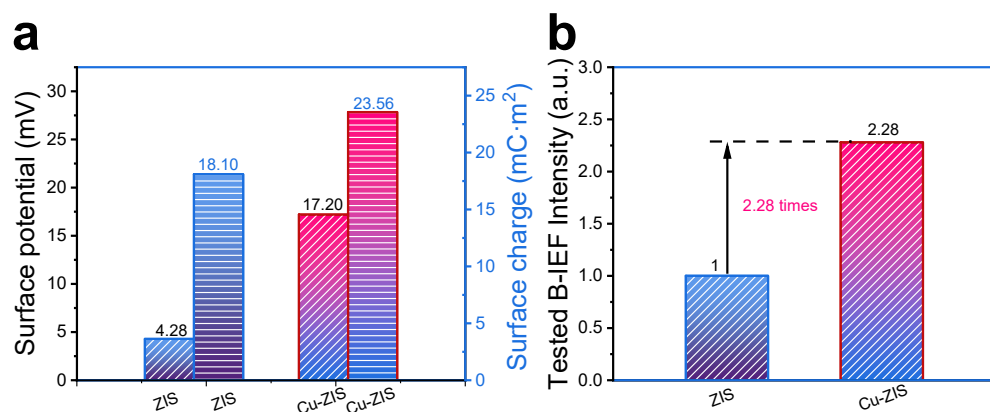


Supplementary Fig. 35. Surface potentials of ZIS and Cu-ZIS. KPFM images at the surface potential mode of (a) ZIS and (b) Cu-ZIS.

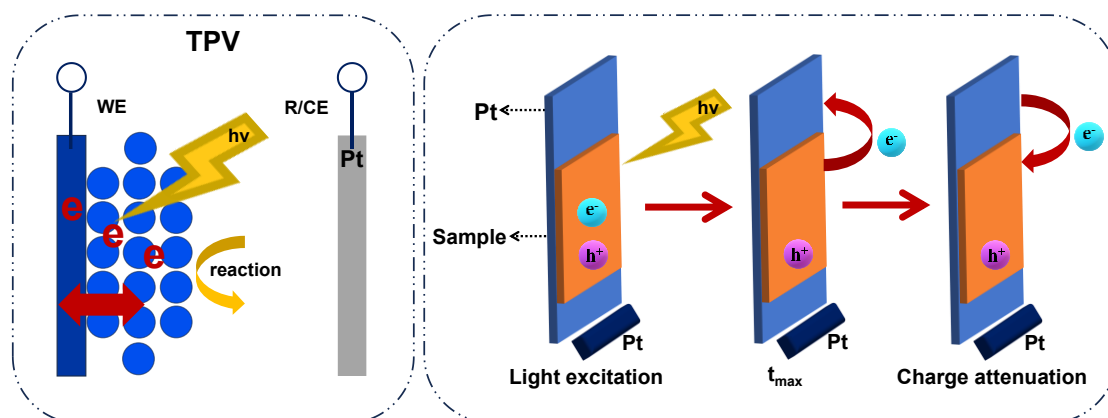


Supplementary Fig. 36. Morphology characterization of ZIS and Cu-ZIS by AFM.

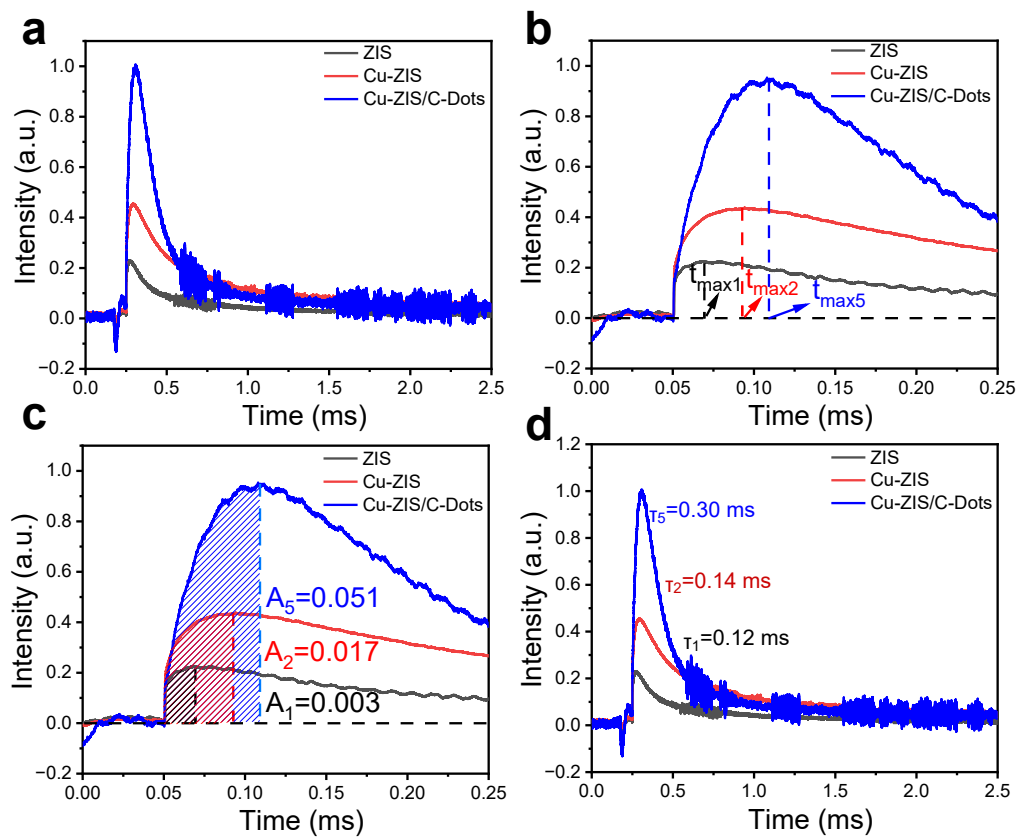
AFM images and the corresponding height profiles of (a) ZIS and (b) Cu-ZIS.



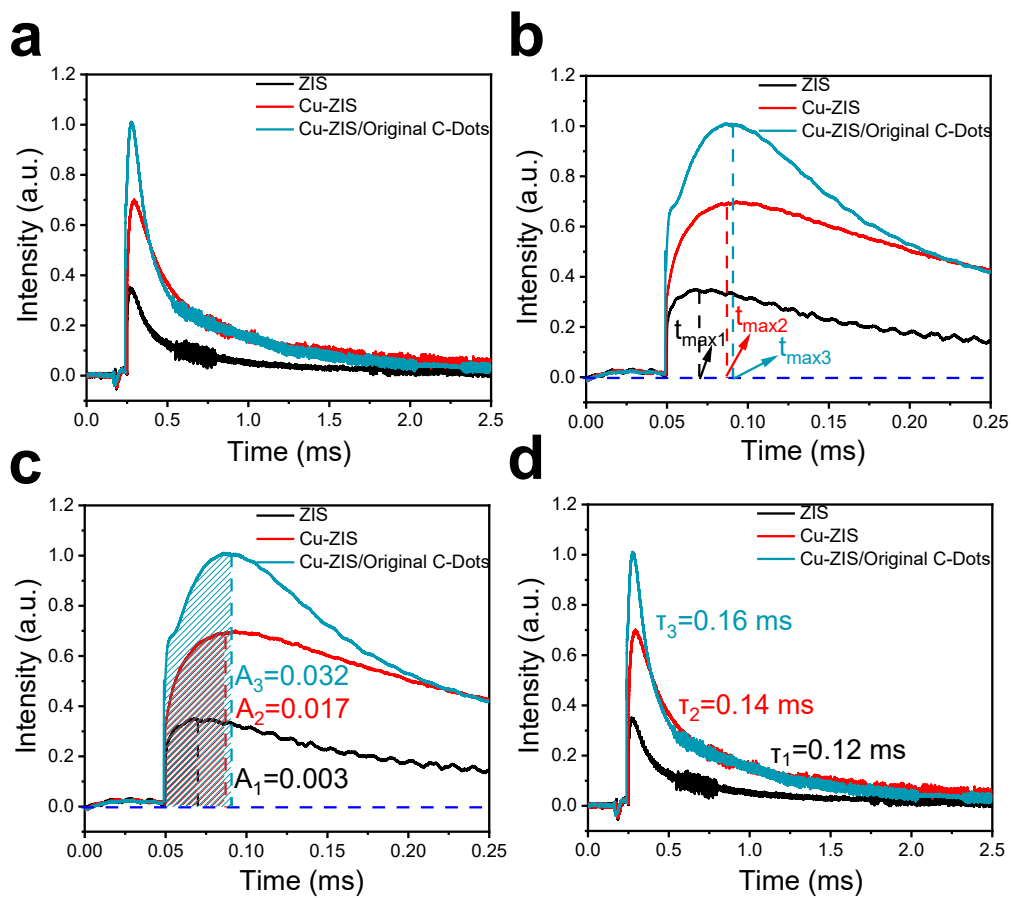
Supplementary Fig. 37. Surface potentials, surface charges, and B-IEF intensity analysis. (a) Surface potentials and calculated surface charges, and (b) tested B-IEF intensity of ZIS and Cu-ZIS nanosheets.



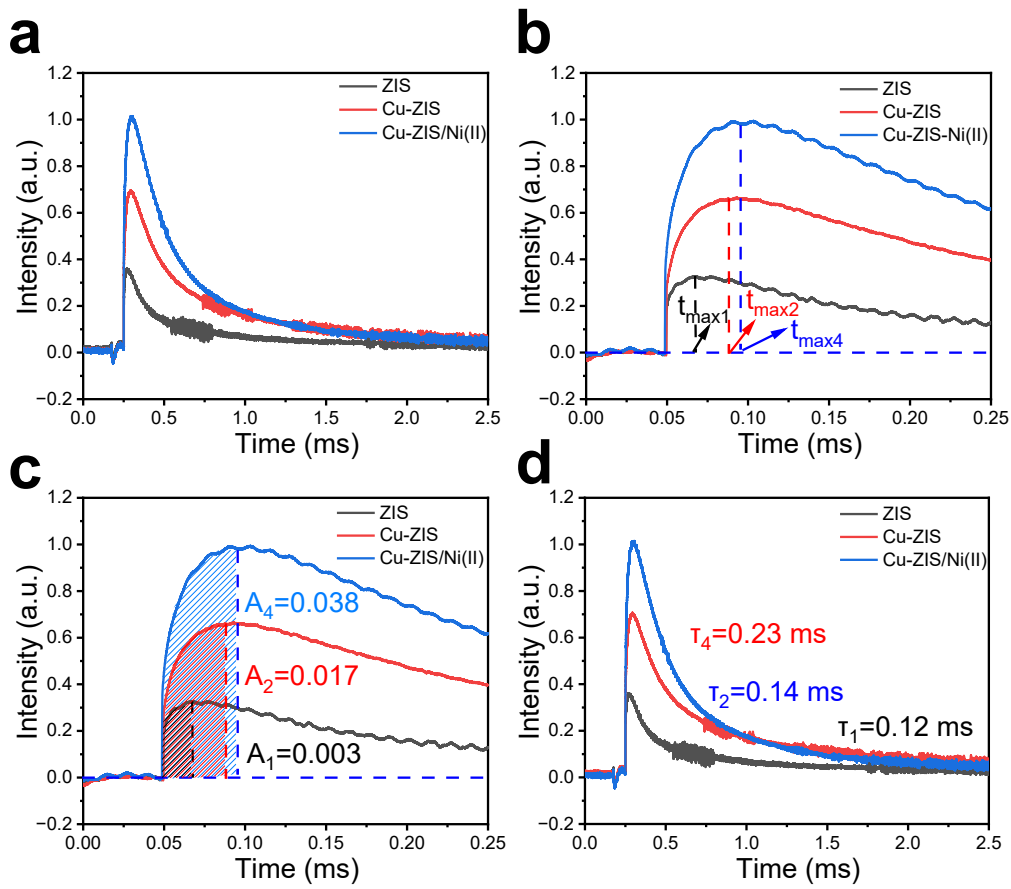
Supplementary Fig. 38. Schematic TPV analysis in photocatalysis. The Schematic diagram of TPV ms dynamics for photocatalysis.



Supplementary Fig. 39. TPV analysis for ZIS, Cu-ZIS, and Cu-ZIS/C-Dots. (a) TPV relaxation curves, (b) the maximum charge extraction time (t_{max}), (c) amount of charge extraction (A) and (d) attenuation constants (τ) of ZIS (τ_1), Cu-ZIS (τ_2) and Cu-ZIS/C-Dots (τ_5) estimated from TPV spectra.

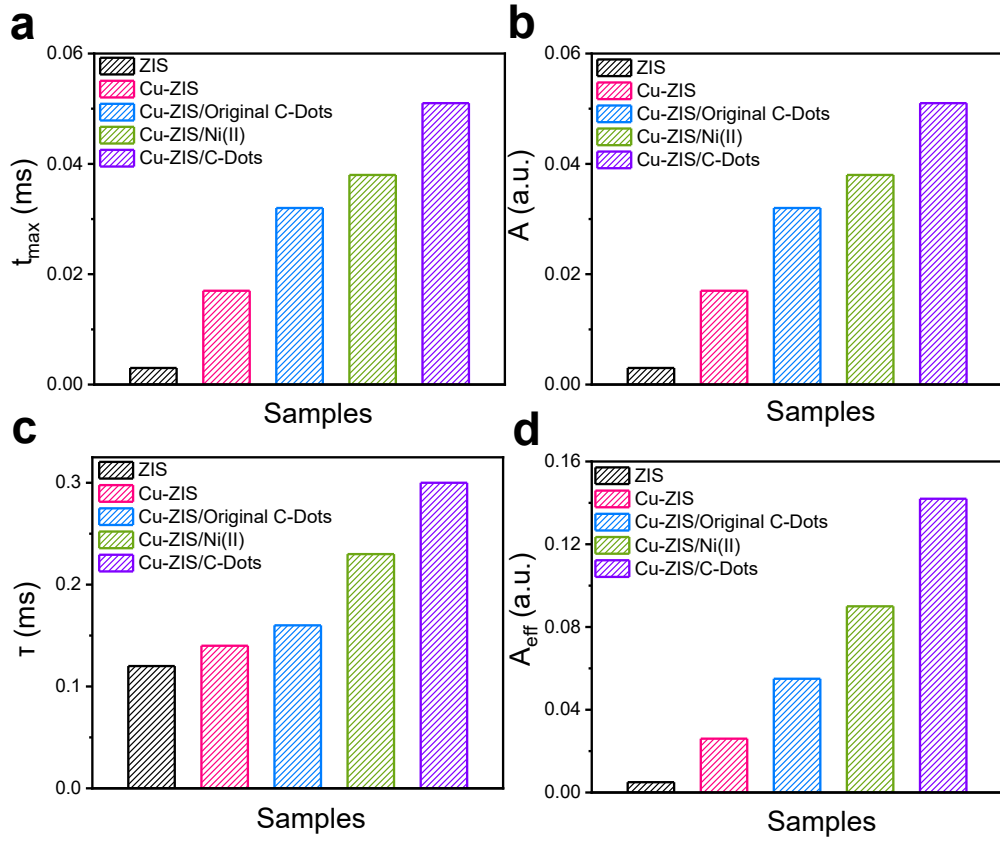


Supplementary Fig. 40. TPV dynamic analysis for ZIS, Cu-ZIS, and Cu-ZIS/Original C-Dots. (a) TPV relaxation curves, (b) the maximum charge extraction time (t_{max}), (c) amount of charge extraction (A) and (d) attenuation constants (τ) of ZIS (τ_1), Cu-ZIS (τ_2) and Cu-ZIS/Original C-Dots (τ_3) estimated from TPV spectra.

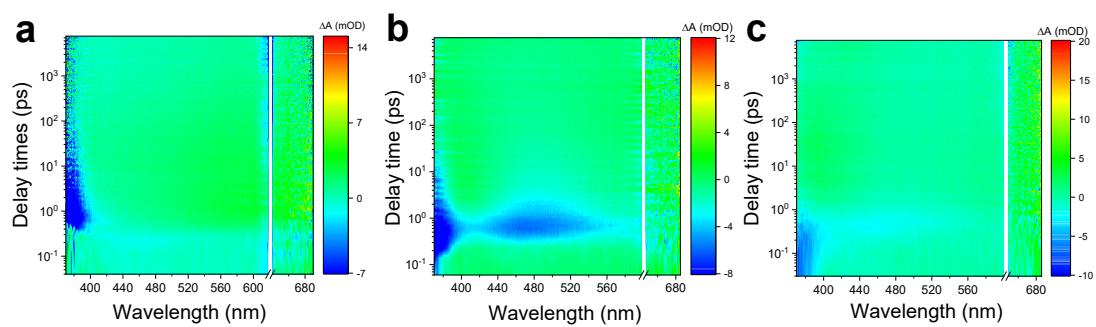


Supplementary Fig. 41. TPV dynamic analysis for ZIS, Cu-ZIS, and Cu-ZIS/Ni(II).

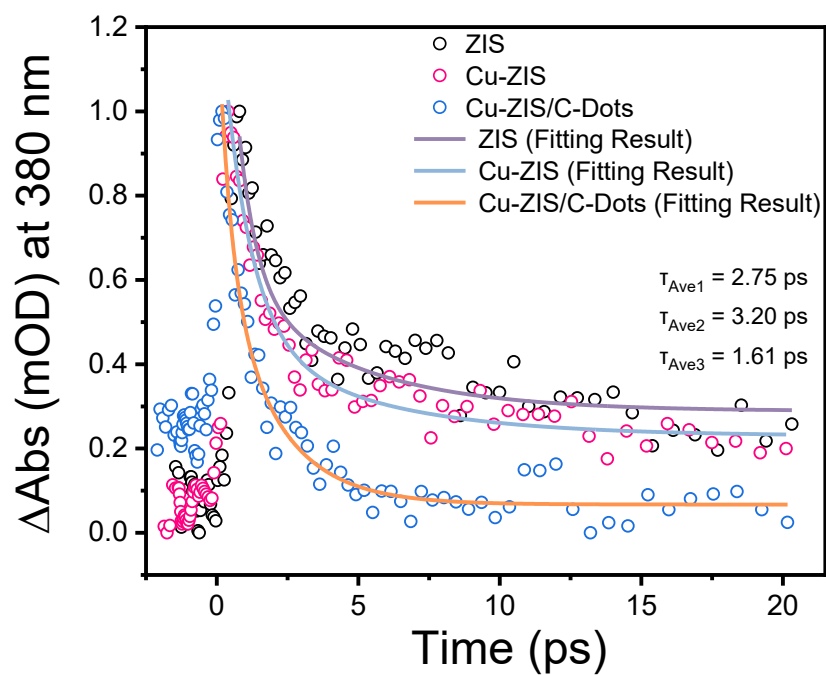
(a) TPV relaxation curves, (b) the maximum charge extraction time (t_{max}), (c) amount of charge extraction (A) and (d) attenuation constants (τ) of ZIS (τ_1), Cu-ZIS (τ_2) and Cu-ZIS/Ni(II) (τ_4) estimated from TPV spectra.



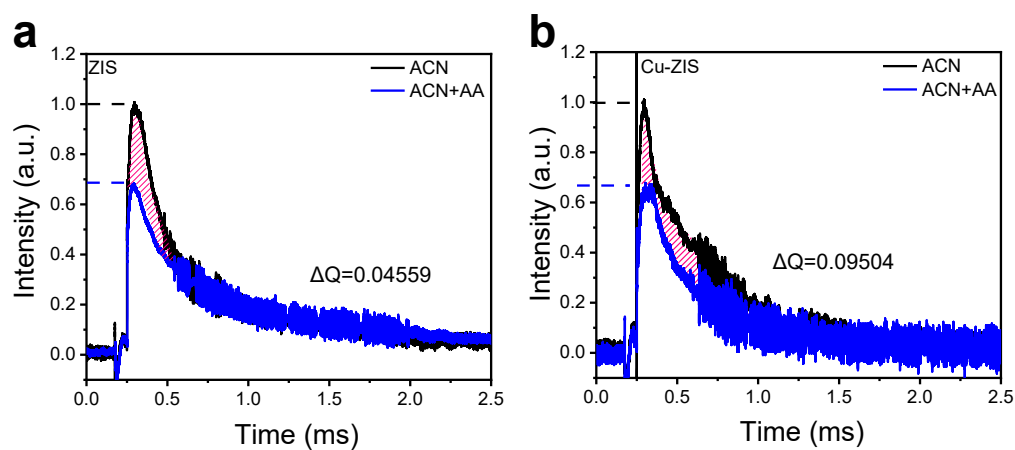
Supplementary Fig. 42. Estimation of effective surface charges. Comparison of (a) t_{max} , (b) A , (c) τ and (d) A_{eff} for ZIS, Cu-ZIS, Cu-ZIS/Original C-Dots, Cu-ZIS/Ni(II) and Cu-ZIS/C-Dots.



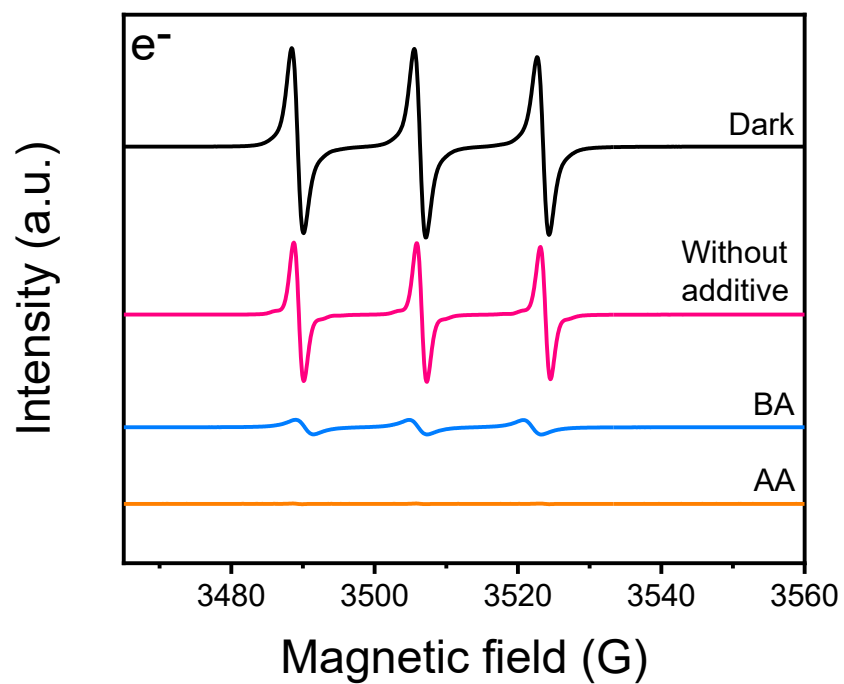
Supplementary Fig. 43. Transient absorption spectra. 3D Color-map plots of the femtosecond ultrafast TAS for (a) ZIS, (b) Cu-ZIS and (c) Cu-ZIS/C-Dots measured under 320-nm pump laser.



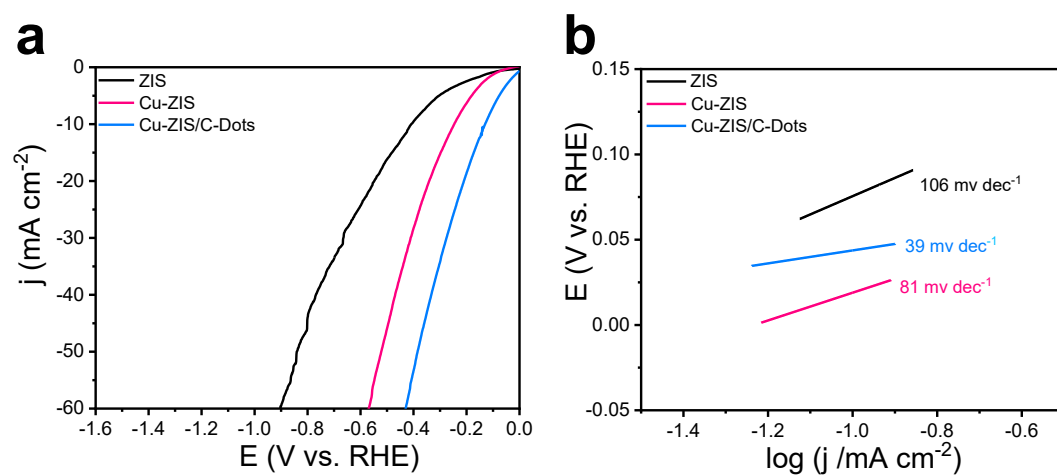
Supplementary Fig. 44. Transient absorption decay curves. The normalized TAS kinetics of ZIS, Cu-ZIS and Cu-ZIS/C-Dots at 380 nm.



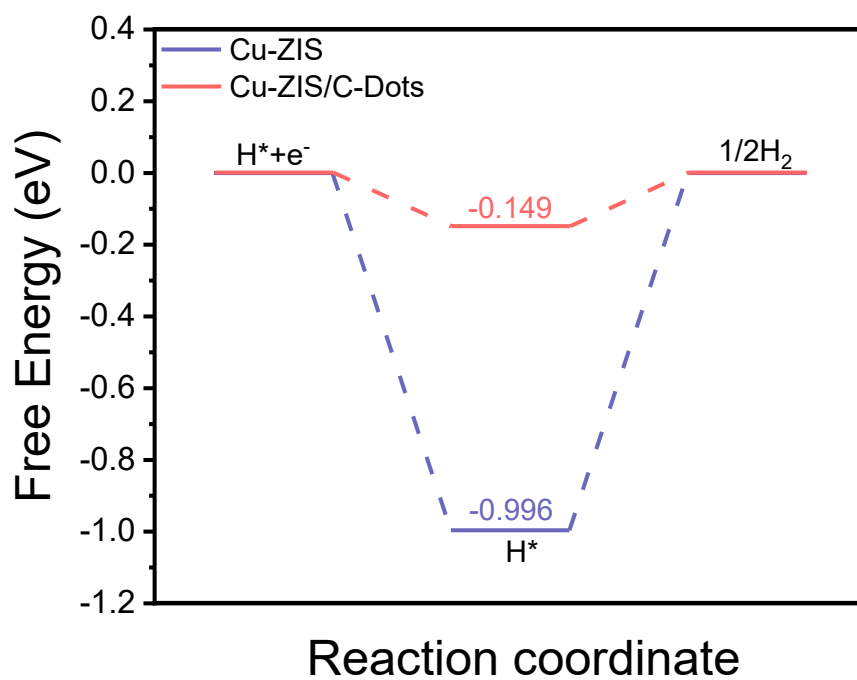
Supplementary Fig. 45. TPV spectra. The in-situ TPV spectra of (a) ZIS and (b) Cu-ZIS with the introduction of ACN and ACN/AA (both containing 5‰ water).



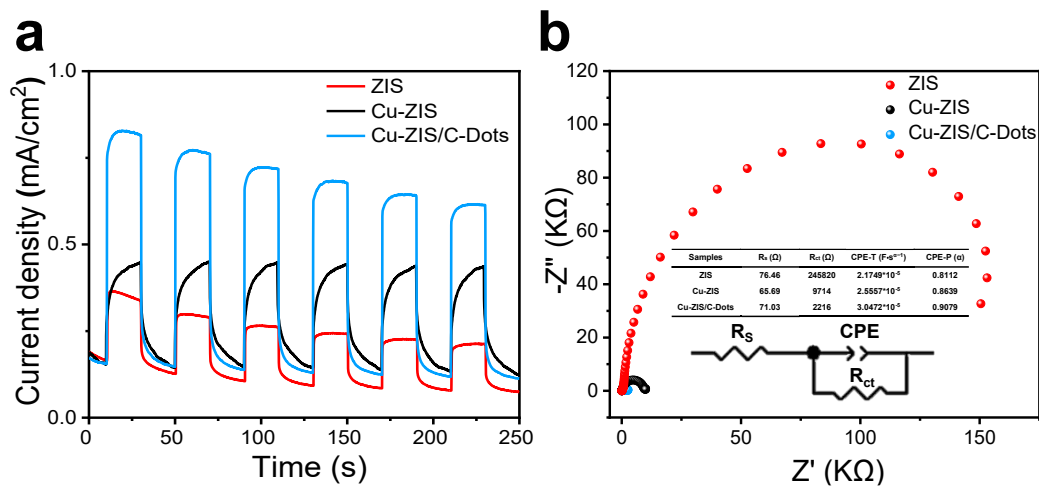
Supplementary Fig. 46. EPR spectra. The *in-situ* EPR spectra of photogenerated electrons by TEMPO spin-label with different additives over Cu-ZIS/C-Dots.



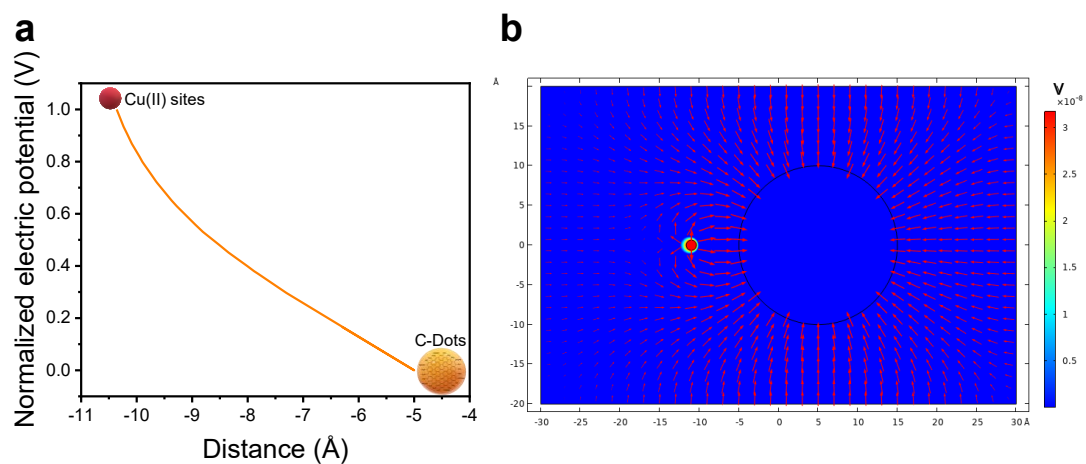
Supplementary Fig. 47. Electrocatalytic HER tests. (a) The electrocatalytic HER activity and (b) Tafel plots of ZIS, Cu-ZIS and Cu-ZIS/C-Dots with light in 1 M PBS.



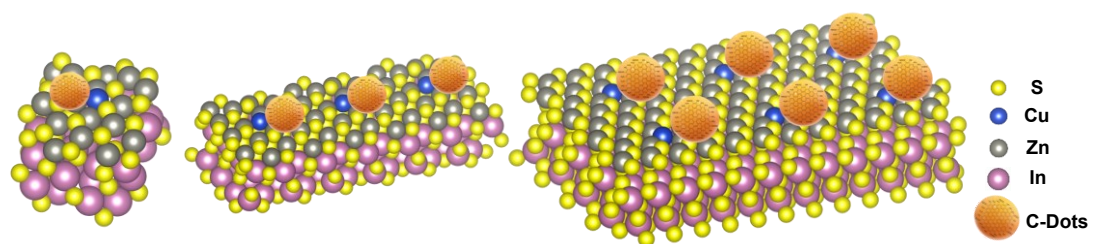
Supplementary Fig. 48. Gibbs free energy. The Gibbs free energy of HER for Cu-ZIS and Cu-ZIS/C-Dots.



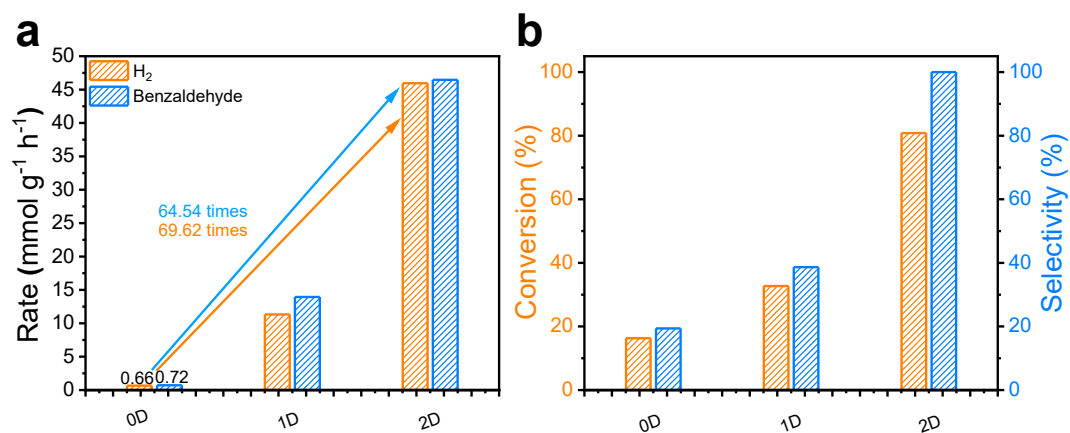
Supplementary Fig. 49. Photocurrent and EIS. (a) Transient photocurrent responses and (b) EIS spectra of ZIS, Cu-ZIS and Cu-ZIS/C-Dots. Inset is an equivalent circuit of EIS. The R_s is the solution resistance, CPE is the capacitance phase element for the semiconductor electrolyte interface. R_{ct} is the charge transfer resistance across the interface^{18,20,21}.



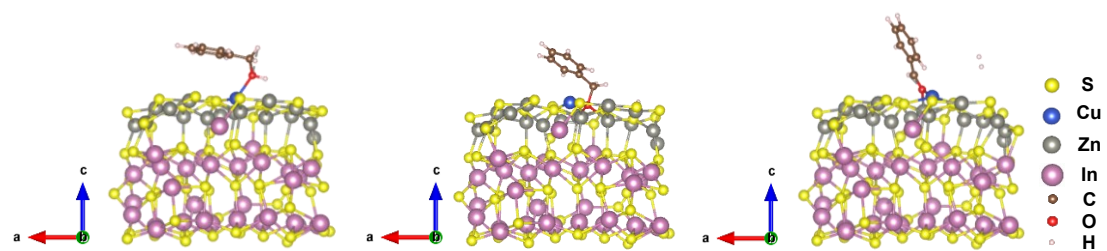
Supplementary Fig. 50. Electric potential results by COMSOL Multiphysics simulation. (a) Curve of potential intensity versus distance from Cu(II) sites to C-Dots. (b) Electric potential distribution of Cu-ZIS/C-Dots.



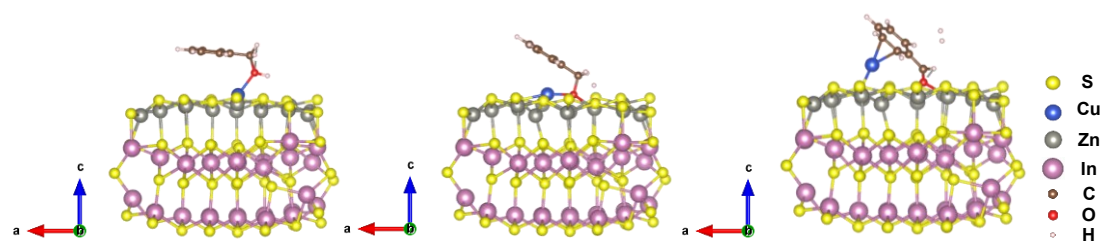
Supplementary Fig. 51. Schematic diagrams for the parallel up of the factory-like nanoreactors loaded on 0D Cu-ZIS QDs, 1D Cu-ZIS nanowires and 2D Cu-ZIS nanosheets.



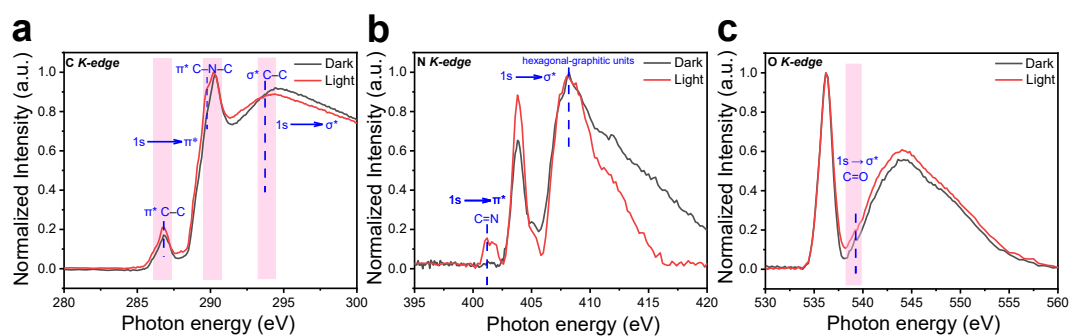
Supplementary Fig. 52. Photocatalytic activities of different shaped catalysts. (a) Comparison of photocatalytic H₂ and BAD production rates and (b) BA conversion and BAD selectivity of 0D Cu-ZIS QDs, 1D Cu-ZIS nanowires and 2D Cu-ZIS nanosheets combined with C-Dots in 5 h.



Supplementary Fig. 53. DFT optimized structures. Side view of the optimized structures of the active intermediates adsorbed on the Cu(II) site for 0D QDs along the Z axis.

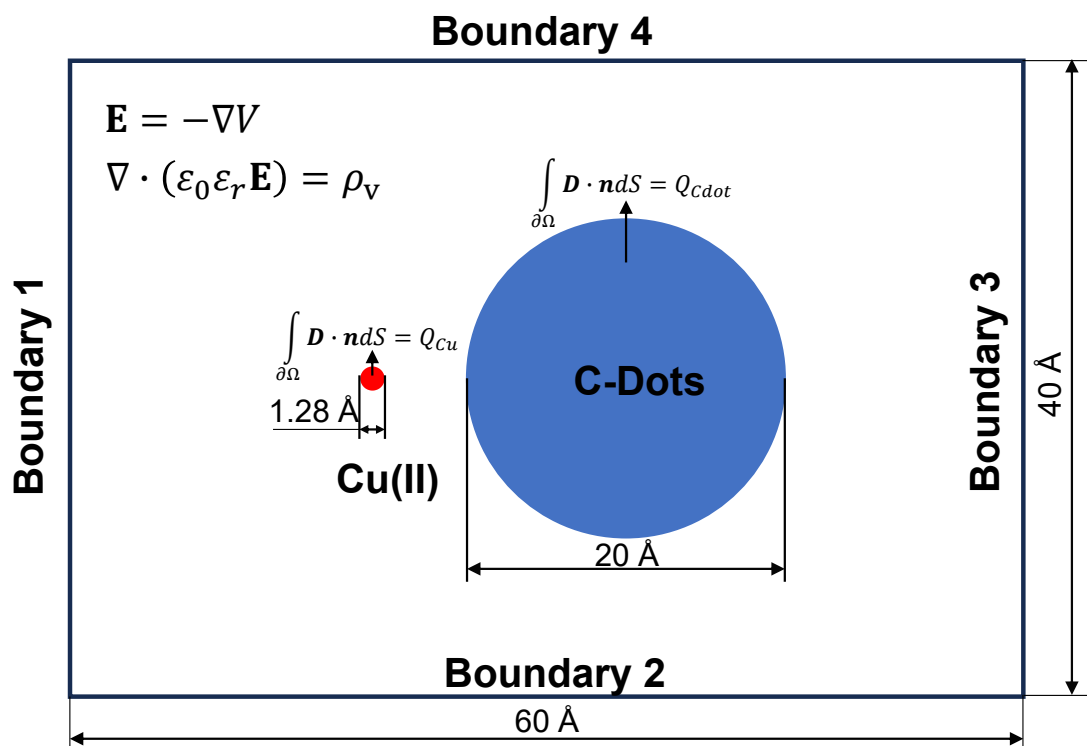


Supplementary Fig. 54. DFT optimized structures. Side view of the optimized structures of the active intermediates adsorbed on the Cu(II) site for 1D nanowires along the Z axis.



Supplementary Fig. 55. XANES analysis of C-Dots. (a) C, (b) N and (c) O K-edge

XANES spectra of C-Dots in the dark and under illumination.



Supplementary Fig. 56. Boundary conditions. The boundary conditions of COMSOL Multiphysics simulation.

Supplementary Tables

Supplementary Table 1. Fitting parameters of the time-resolved PL spectra of the samples.

Samples	A ₁	τ_1 (ns)	A ₂	τ_2 (ns)	τ_{ave} (ns)
ZIS	5.29*10 ⁷	16.96	10606.81	77.14	17.21
Cu-ZIS	3.25*10 ⁸	13.60	3504.80	83.35	13.63
Cu-ZIS/C-Dots	2.69*10 ¹⁷	4.66	172163.25	28.34	4.67

The time-resolved PL decay curves for all the samples were fitted with bi-exponential function based on the following expression^{22,23}

$$\text{Fit} = A + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

where A₁ and A₂ are fractional contributions, and τ_1 and τ_2 are the corresponding PL lifetimes of different decay components. And the average lifetime τ_{ave} could be calculated from Equation: $\tau_{ave} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$.

Supplementary Table 2. Calculation of the apparent quantum efficiency (AQE) at different wavelengths for BA system.

Wavelength	H₂ Production	Light Intensity	AQE
$\lambda = 420$ nm	513.52 μmol	67.7 mW	39.99%
$\lambda = 450$ nm	413.98 μmol	76.5 mW	26.62%
$\lambda = 485$ nm	275.59 μmol	69.4 mW	18.13%
$\lambda = 520$ nm	94.57 μmol	50.2 mW	8.02%
$\lambda = 595$ nm	22.87 μmol	20.2 mW	4.21%
$\lambda = 630$ nm	7.43 μmol	42.6 mW	0.61%

Supplementary Table 3. Calculation of the apparent quantum efficiency (AQE) at different wavelengths for AA system.

Wavelength	H₂ Production	Light Intensity	AQE
$\lambda = 420$ nm	1089.71 μmol	67.7 mW	84.86%
$\lambda = 450$ nm	817.20 μmol	76.5 mW	52.56%
$\lambda = 485$ nm	480.06 μmol	69.4 mW	31.59%
$\lambda = 520$ nm	176.74 μmol	50.2 mW	15.01%
$\lambda = 595$ nm	35.88 μmol	20.2 mW	6.61%
$\lambda = 630$ nm	8.38 μmol	42.6 mW	0.69%

Supplementary Table 4. Activity comparison of the selective photocatalytic oxidation of BA into BAD and H₂ over various photocatalysts reported in literatures.

Photocatalyst	Mass (mg)	Sel. (%)	H ₂ (μmol g ⁻¹ h ⁻¹)	Light source	Time (h)	Ref.
ZnS/Ni _x S _y	20	90.5	2943.0	500 W Xe lamp (λ ≥ 420 nm)	3	24
WO ₃ /ZnIn ₂ S ₄	10	94.8	4280.0	300 W Xe lamp (λ ≥ 420 nm)	5	25
0.03-MoS _x /Zn ₃ In ₂ S ₆	20	96.2	5180.0	300 W Xe lamp (λ ≥ 420 nm)	1	26
Cd _{0.5} Zn _{0.5} S/Ti ₃ C ₂	25	99.0	5300.0	300 W Xe lamp (λ ≥ 400 nm)	20	27
Ru/g-C ₃ N ₄	5	99.0	6420.0	300 W Xe lamp (850 nm > λ > 320 nm)	3	28
ZnIn ₂ S ₄ /Ni _x -B	10	96.0	8900.0	300 W Xe lamp (λ ≥ 400 nm)	2	29
Co/CdS	5	-	8940.0	300 W Xe lamp (λ ≥ 420 nm)	3	30
PAZ-1 (HPM/ZIS)	5	98.2	10600.0	300 W Xe lamp (λ ≥ 420 nm)	5	31
NP/ZIS-O	30	-	15790.0	300 W Xe lamp (780 nm > λ > 300 nm)	3	32
VC/CdS	25	99.0	20500.0	300 W Xe lamp (λ ≥ 420 nm)	2	33
^{NCN} CN _x -NiP	5	100.0	21.47	300 W Xe lamp (λ ≥ 400 nm)	24	34
^{NCN} CN _x -GO-NiP	5	100.0	7.19	AM 1.5G, 100 mW cm ⁻²	4	35
Ni/Zn _{0.5} Cd _{0.5} S	5	57.7	284.8	300 W Xe lamp (λ ≥ 420 nm)	3	36
Cu-ZIS/C-Dots	10	near-unity selectivity (≈ 100.0)	45950	100 W LED light (λ ≥ 420 nm)	5	This work

Supplementary Table 5. Comparison of activity of hydrogen production using sacrificial reagents of Cu-ZIS/C-Dots compared the related photocatalysts.

Catalysts	Light Source	Reaction Conditions	H ₂ Evolution Rate (mmol g ⁻¹ h ⁻¹)	Ref.
Cu-ZIS/C-Dots	$\lambda \geq 420$ nm	0.2 M L-ascorbic acid	98.84	This work
		(AA)		
Cu ₂ ZnSnS ₄	$\lambda \geq 420$ nm	0.35 M Na ₂ S + 0.25 M Na ₂ SO ₃	0.381	3
Cu-ZIS	$\lambda \geq 420$ nm	0.2 M L-ascorbic acid	9.86	37
NiPS ₃ /Original C-Dots	$\lambda \geq 420$ nm	Aqueous TEOA solution (17%)	13.60	38
Original C-Dots	300 W Xenon lamp	Aqueous TEOA solution (10%)	19.70	39
Pt/Original C-Dots	$\lambda \geq 420$ nm	lactic acid (20%)	19.77	40
Cu _{0.5} -ZIS	$\lambda \geq 420$ nm	lactic acid (20%)	26.20	41
Pt _{0.3} -ZIS	Simulated solar light	0.35 M Na ₂ S + 0.25 M Na ₂ SO ₃	29.20	42
Rh/Cr ₂ O ₃ /CoOOH/SrTiO ₃ :Al	$\lambda \geq 420$ nm	Aqueous TEOA solution (10%)	35.40	43
RhCrO _x /SrTiO ₃ :Al	$\lambda \geq 420$ nm	0.2 M L-ascorbic acid	37.50	44
MoSe ₂ /ZIS	$\lambda \geq 420$ nm	Aqueous TEOA solution (10%)	63.21	45

Supplementary Table 6. Bi-exponential fitting components of the transient absorption spectra of ZIS, Cu-ZIS and Cu-ZIS/C-Dots under 320 nm pump excitation monitored at 380 nm.

Samples		A_1	A_2	τ_1 (ps)	τ_2 (ps)	τ_{ave} (ps)
ZIS	380 nm	0.369	0.631	0.65	4.15	2.75
Cu-ZIS	380 nm	0.404	0.596	0.97	4.71	3.20
Cu-ZIS/C-Dots	380 nm	0.185	0.815	0.44	1.88	1.61

The TAS decay curves for all the samples were fitted with a bi-exponential function based on the following expression.

$$I(t) = y_0 + A_1 * \exp(-(t - t_0)/\tau_1) + A_2 * \exp(-(t - t_0)/\tau_2) \quad (1)$$

where A_1 and A_2 are fractional contributions, and τ_1 and τ_2 are the corresponding TAS lifetimes of different decay components. And the average lifetime τ_{ave} can be calculated from Equation^{46,47} (2):

$$\tau_{ave} = [-\int_0^\infty t \frac{d}{dt} \left(\frac{I(t)-y_0}{I(0)-y_0} \right) dt = \int_0^\infty \left(\frac{I(t)-y_0}{I(0)-y_0} \right) dt] \quad (2)$$

Supplementary Table 7. The DFT calculated Bader charges of Cu-ZIS/C-Dots.

C-Dots Atoms	Coordinates (Å)			Charge (e)	Charge difference (e)
	X	Y	Z		
Cu	6.867414	5.658628	17.273828	11.173442	0.173
In	0.963453	4.511145	8.935555	11.872386	-1.128
In	0.966124	11.297199	8.939351	11.878017	-1.122
In	8.823638	4.515351	8.949222	11.89195	-1.108
In	8.824738	11.29747	8.94745	11.88565	-1.114
In	4.896452	4.51508	8.948209	11.88878	-1.111
In	4.894095	11.296928	8.942388	11.882815	-1.117
In	12.747682	4.513316	8.940617	11.877746	-1.122
In	12.750667	11.300727	8.945425	11.881459	-1.119
In	0.969738	2.256861	12.976486	11.709337	-1.291
In	0.974923	9.052551	12.990912	11.713617	-1.286
In	8.861189	2.244377	12.969146	11.709448	-1.291
In	8.846735	9.072363	12.988634	11.7104	-1.29
In	4.894724	2.250076	12.960794	11.711921	-1.288
In	4.898495	9.07657	12.972689	11.709881	-1.29
In	12.775335	2.253469	12.982813	11.709975	-1.29
In	12.770464	9.044001	12.998252	11.712209	-1.288
In	2.942836	1.11805	8.928974	11.832257	-1.168
In	2.94425	7.906818	8.940363	11.881041	-1.119
In	10.801136	1.123749	8.928721	11.834097	-1.166
In	10.806949	7.908039	8.952006	11.892842	-1.107
In	6.874264	1.11805	8.934036	11.873527	-1.126
In	6.877878	7.903833	8.949728	11.896936	-1.103
In	14.72518	1.119135	8.92619	11.837496	-1.163
In	14.728479	7.906682	8.940617	11.878729	-1.121
In	2.921311	5.657284	12.981041	11.709946	-1.29
In	2.935609	12.440353	12.998252	11.710968	-1.289
In	10.827061	5.649821	12.988887	11.7086	-1.291
In	10.808363	12.435197	12.997239	11.712631	-1.287
In	6.881335	5.662577	12.955985	11.708327	-1.292
In	6.87285	12.453245	12.994962	11.709485	-1.291
In	14.729108	5.654435	12.994962	11.711837	-1.288
In	14.727065	12.43574	12.986103	11.71159	-1.288
S	4.91339	2.292212	17.455526	6.851632	0.852
S	4.941875	9.068957	17.464333	6.860934	0.861
S	12.757517	2.268193	17.45998	6.880406	0.88
S	12.773606	9.057165	17.302352	6.8882	0.888
S	2.935923	3.384546	7.796116	6.79899	0.799
S	2.932309	10.166801	7.794092	6.798847	0.799
S	10.781025	3.386717	7.792573	6.79974	0.8
S	10.785738	10.166393	7.800672	6.799852	0.8
S	0.994987	2.270147	17.442491	6.874841	0.875
S	0.98314	9.045101	17.465194	6.898208	0.898
S	8.867459	2.292809	17.477216	6.873319	0.873
S	8.823921	9.076176	17.380179	6.866418	0.866

S	0.976494	4.51603	11.391851	6.868335	0.868
S	0.983093	11.301949	11.392358	6.864026	0.864
S	8.839821	4.522272	11.414124	6.850182	0.85
S	8.830866	11.312805	11.403494	6.858185	0.858
S	4.910593	4.527565	11.412352	6.848987	0.849
S	4.91185	11.319047	11.399444	6.860215	0.86
S	12.763708	4.511823	11.394889	6.865781	0.866
S	12.759623	11.297335	11.397673	6.862	0.862
S	2.94535	3.393231	14.219693	6.801098	0.801
S	2.942993	10.179285	14.236904	6.802392	0.802
S	10.80035	3.390924	14.231082	6.820289	0.82
S	10.801765	10.178064	14.241712	6.793499	0.793
S	6.874893	3.396759	14.223236	6.830428	0.83
S	6.868608	10.182542	14.234626	6.80937	0.809
S	14.727851	3.393909	14.226527	6.806223	0.806
S	14.727379	10.182406	14.232348	6.800852	0.801
S	6.860438	3.385496	7.802444	6.799278	0.799
S	6.861695	10.16273	7.804215	6.799344	0.799
S	14.709782	3.384003	7.787258	6.800779	0.801
S	14.712139	10.167208	7.79561	6.800781	0.801
S	2.95319	5.648369	17.433354	6.858232	0.858
S	2.958815	12.450884	17.467219	6.878264	0.878
S	10.817586	5.641652	17.325839	6.871547	0.872
S	10.800822	12.445768	17.477267	6.892212	0.892
S	6.885121	12.458022	17.454893	6.891764	0.892
S	14.742557	5.658438	17.452286	6.890856	0.891
S	14.733413	12.433202	17.459398	6.88863	0.889
S	2.942208	1.122121	11.386283	6.910576	0.911
S	2.955249	7.909939	11.399444	6.861557	0.862
S	10.806635	1.121035	11.38603	6.911831	0.912
S	10.793437	7.904918	11.409821	6.850909	0.851
S	6.878507	1.138133	11.394129	6.868549	0.869
S	6.878664	7.920252	11.413871	6.848219	0.848
S	14.728479	1.118321	11.380968	6.904476	0.904
S	14.729422	7.903833	11.395395	6.866503	0.867
S	0.976179	0.004885	14.223996	6.799765	0.8
S	0.981993	6.792432	14.232854	6.829363	0.829
S	8.837936	0.006514	14.232854	6.817067	0.817
S	8.836993	6.788226	14.241712	6.820241	0.82
S	4.90745	0.012349	14.228298	6.804918	0.805
S	4.916249	6.793382	14.23007	6.825636	0.826
S	12.766064	0.00285	14.227539	6.806126	0.806
S	12.767793	6.785919	14.240953	6.789907	0.79
S	0.980579	6.773841	7.793839	6.797392	0.797
S	0.979165	13.554468	7.782955	6.800352	0.8
S	8.841707	6.77452	7.806746	6.796588	0.797
S	8.835736	13.553246	7.79232	6.799334	0.799
S	4.913421	6.774248	7.803709	6.794912	0.795
S	4.909336	13.554875	7.790042	6.799372	0.799
S	12.762765	6.774113	7.796369	6.797942	0.798

S	12.758994	13.55501	7.782702	6.799874	0.8
Zn	2.93707	3.386174	16.941893	11.119413	-0.881
Zn	2.946387	10.191756	17.087651	11.127956	-0.872
Zn	10.833015	3.375196	16.860725	11.112541	-0.887
Zn	10.810705	10.204119	16.94207	11.140599	-0.859
Zn	6.888531	3.174628	16.764523	11.253841	-0.746
Zn	6.86567	10.225777	16.903599	11.122071	-0.878
Zn	14.735047	3.380149	17.066745	11.113441	-0.887
Zn	14.751544	10.193154	16.961634	11.13116	-0.869
Zn	0.984255	0.004003	17.097167	11.123201	-0.877
Zn	0.988325	6.79155	16.982666	11.116078	-0.884
Zn	8.849955	0.009065	17.037006	11.122472	-0.878
Zn	9.002471	6.890477	16.761865	11.26505	-0.735
Zn	4.723684	6.912922	16.776596	11.265735	-0.734
Zn	4.910891	0.010151	17.073047	11.120356	-0.88
Zn	12.797991	6.790709	16.942702	11.144597	-0.855
Zn	12.77854	0.004302	17.068263	11.12204	-0.878
C	8.596287	6.594606	20.919803	4.012033	0.012
C	9.270626	5.382203	20.813755	3.93857	-0.061
C	10.670319	5.350516	20.761567	3.607112	-0.393
C	8.623767	9.083667	20.976091	4.115521	0.116
C	9.302489	7.816712	20.957337	3.966824	-0.033
C	10.72707	7.790155	20.90363	4.01541	0.015
C	11.437687	6.560938	20.813755	4.011257	0.011
C	12.840539	6.559961	20.721375	3.989044	-0.011
C	9.329639	10.309193	20.74094	4.033267	0.033
C	10.742814	10.262756	20.969409	4.188022	0.188
C	11.471059	9.011989	20.930281	3.952758	-0.047
C	12.86706	8.981294	20.842558	4.057861	0.058
C	13.56979	7.76296	20.704544	3.517119	-0.483
H	13.419962	9.92274	20.812642	0.905029	-0.095
H	13.366274	5.612001	20.609406	0.902331	-0.098
H	8.714645	4.445126	20.737548	0.915825	-0.084
H	11.319235	11.188637	20.897555	0.884975	-0.115
H	7.532325	9.082269	20.926079	0.902312	-0.098
H	7.505175	6.60724	20.929294	0.947159	-0.053
H	15.37562	8.588517	20.198327	0.541835	-0.458
H	15.319764	6.907141	20.137736	0.525161	-0.475
H	8.820056	11.224286	20.433605	0.890909	-0.109
H	10.769681	3.452465	20.453245	0.350793	-0.649
N	14.938484	7.747042	20.567518	6.222244	1.222
O	11.365098	4.199016	20.659772	7.127639	1.128
Ni	9.551774	9.944276	22.58806	9.566881	-0.433
Cu(II) Total					0.173
C-Dots Total					-0.912

Supplementary Table 8. Parameters and boundary conditions used in COMSOLMultiphysics simulation⁴⁸⁻⁵⁰.

Physical parameters	Value
Density of Cu(II) (kg/m ³)	8939.81
Density of hydrogen (kg/m ³)	0.0837
Density of C-Dots (kg/m ³)	790.00
Size of Cu(II) (Å)	1.28
Size of C-Dots (nm)	2
Relative permittivity of water	80.1
Relative permittivity of Cu(II)	6
Relative permittivity of C-Dots	1.5
Porosity of nanosheet	0.15
Diffusion coefficient of hydrogen (m ² /s)	9.31×10^{-9}
Boundary conditions	Descriptions
Boundaries 1,2,3,4	Potential $V=0$; No flux
Cu(II)	Charge $Q_0 = 0.28 \times 10^{-19}$ (C); Concentration 1, Dimensionless $c_H = 1$ $\int_{\partial\Omega} \mathbf{D} \cdot \mathbf{n} dS = Q_{Cu(II)}$
C-Dots	Charge $Q_0 = -1.46 \times 10^{-19}$ (C); Concentration 2, Dimensionless $c_H = 0$ $\int_{\partial\Omega} \mathbf{D} \cdot \mathbf{n} dS = Q_{C-Dots}$

Supplementary Table 9. The DFT calculated ZPE energies of different intermediates

on the Cu-ZnIn₂S₄ nanosheets.

Intermediate	E _{tot} (eV)	TS (eV)	ZPE (eV)	G (eV)
*RCH ₂ OH	-521.3276	0.1493	3.5466	-517.9303
*RCH ₂ O	-522.3090	0.1450	3.4562	-518.9978
*RCHO	-521.8522	0.2571	3.2689	-518.8404
*	-421.8745	0.0000	0.0000	-412.8745

Supplementary Table 10. The DFT calculated energies of E_{ads} , E_{sub} and E_{tot} with different distances from Cu(II) to the center of C-Dots.

Distance	E_{ad} (eV)	E_{sub} (eV)	E_{tot} (eV)
5.7 Å	-171.42232	-422.19608	-595.49075
8.9 Å	~	~	-595.44137

Supplementary References

1. Luo B, *et al.* A periplasmic photosensitized biohybrid system for solar hydrogen production. *Adv. Energy Mater.* **11**, 2100256 (2021).
2. Sun X, Zhao L, Cheng J, Fang Z, Zhou H, Li S. Regulation of Charge Transfer Pathway in Ag-ZnIn₂S₄ Nanowires for Visible Photodynamic Therapy on Candida Albicans Infections. *Small*, 2400867 (2024).
3. Wang Y, *et al.* Carbon quantum dot implanted graphite carbon nitride nanotubes: excellent charge separation and enhanced photocatalytic hydrogen evolution. *Angew. Chem. Int. Ed.* **57**, 5765-5771 (2018).
4. Yan X, *et al.* An electron-hole rich dual-site nickel catalyst for efficient photocatalytic overall water splitting. *Nat. Commun.* **14**, 1741 (2023).
5. Wu Q, *et al.* A metal-free photocatalyst for highly efficient hydrogen peroxide photoproduction in real seawater. *Nat. Commun.* **12**, 483 (2021).
6. Wei K, *et al.* Simple Semiempirical Method for the Location Determination of HOMO and LUMO of Carbon Dots. *J. Phys. Chem. C* **125**, 7451-7457 (2021).
7. Luo Y, Chang Z, Pei J, Guo Z, Zhan H. Design, Synthesis, and Ultrafast Carrier Dynamics of Core-Substituted Naphthalene Diimide-Based Covalent Organic Frameworks. *Nano Lett.* **23**, 9266-9271 (2023).
8. Matsumura Y, *et al.* Arsole-Containing π -Conjugated Polymer by the Post-Element-Transformation Technique. *Angew. Chem. Int. Ed.* **55**, 15040-15043 (2016).
9. Cao S, Shen B, Tong T, Fu J, Yu J. 2D/2D Heterojunction of Ultrathin

- MXene/Bi₂WO₆ Nanosheets for Improved Photocatalytic CO₂ Reduction. *Adv. Funct. Mater.* **28**, 1800136 (2018).
10. Perdew JP, Ernzerhof M, Burke K. Rationale for mixing exact exchange with density functional approximations. *J. Chem. Phys.* **105**, 9982-9985 (1996).
 11. Perdew JP, Burke K, Ernzerhof M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
 12. Zhu Y, *et al.* In Situ Topochemical Transformation of ZnIn₂S₄ for Efficient Photocatalytic Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran. *Adv. Funct. Mater.* **33**, 2304985 (2023).
 13. Chong W-K, *et al.* Self-activated superhydrophilic green ZnIn₂S₄ realizing solar-driven overall water splitting: close-to-unity stability for a full daytime. *Nat. Commun.* **14**, 7676 (2023).
 14. Reuter K, Scheffler M. Composition, structure, and stability of RuO₂(110) as a function of oxygen pressure. *Phys. Rev. B* **65**, 035406 (2001).
 15. Xu X-L, Chen Z-H, Li Y, Chen W-K, Li J-Q. Bulk and surface properties of spinel Co₃O₄ by density functional calculations. *Surf Sci* **603**, 653-658 (2009).
 16. Zasada F, Gryboś J, Piskorz W, Sojka Z. Cobalt Spinel (111) Facets of Various Stoichiometry—DFT+U and Ab Initio Thermodynamic Investigations. *J. Phys. Chem. C* **122**, 2866-2879 (2018).
 17. Verma KC, Kotnala RK. Defects due to lattice distortion and nano-size intermediate ferromagnetism in La, Gd substituted Zn_{0.95}Co_{0.05}O. *Curr Appl Phys* **16**, 175-182 (2016).

18. Wang P, *et al.* Atomic Insights for Optimum and Excess Doping in Photocatalysis: A Case Study of Few-Layer Cu-ZnIn₂S₄. *Adv. Funct. Mater.* **29**, 1807013 (2019).
19. Pang E, *et al.* Carbon dots induce abundant oxygen vacancies in CeVO₄ for promoting photocatalytic selective hydrogenation of functionalized nitroarenes. *Inorg. Chem. Front.* **11**, 2128-2135 (2024).
20. Shi X, *et al.* Protruding Pt single-sites on hexagonal ZnIn₂S₄ to accelerate photocatalytic hydrogen evolution. *Nat. Commun.* **13**, 1287 (2022).
21. Jo WJ, *et al.* Phosphate Doping into Monoclinic BiVO₄ for Enhanced Photoelectrochemical Water Oxidation Activity. *Angew. Chem. Int. Ed.* **51**, 3147-3151 (2012).
22. Yu S, *et al.* Efficient photocatalytic hydrogen evolution with ligand engineered all-inorganic InP and InP/ZnS colloidal quantum dots. *Nat. Commun.* **9**, 4009 (2018).
23. Xie Z, *et al.* Well-defined diatomic catalysis for photosynthesis of C₂H₄ from CO₂. *Nat. Commun.* **15**, 2422 (2024).
24. Hao H, Zhang L, Wang W, Qiao S, Liu X. Photocatalytic Hydrogen Evolution Coupled with Efficient Selective Benzaldehyde Production from Benzyl Alcohol Aqueous Solution over ZnS-Ni_xS_y Composites. *ACS Sustain. Chem. Eng.* **7**, 10501-10508 (2019).
25. Li Y-H, Qi M-Y, Tang Z-R, Xu Y-J. Coupling Organic Synthesis and Hydrogen Evolution over Composite WO₃/ZnIn₂S₄ Z-Scheme Photocatalyst. *J. Phys.*

- Chem. C* **126**, 1872-1880 (2022).
26. Jing L, *et al.* Multifunctional 3D MoS_x/Zn₃In₂S₆ nanoflower for selective photothermal-catalytic biomass oxidative and non-selective organic pollutants degradation. *Appl. Catal. B* **318**, 121814 (2022).
 27. Tao J, *et al.* Efficient photocatalytic hydrogen evolution coupled with benzaldehyde production over 0D Cd_{0.5}Zn_{0.5}S/2D Ti₃C₂ Schottky heterojunction. *J. Adv. Ceram.* **11**, 1117-1130 (2022).
 28. Yang Q, Wang T, Zheng Z, Xing B, Li C, Li B. Constructing interfacial active sites in Ru/g-C₃N_{4-x} photocatalyst for boosting H₂ evolution coupled with selective benzyl-alcohol oxidation. *Appl. Catal. B* **315**, 121575 (2022).
 29. Li X, *et al.* Ultrathin Two-Dimensional ZnIn₂S₄/Ni_x-B Heterostructure for High-Performance Photocatalytic Fine Chemical Synthesis and H₂ Generation. *ACS Appl. Mater. Interfaces* **14**, 25297-25307 (2022).
 30. Jiang D, *et al.* Highly efficient simultaneous hydrogen evolution and benzaldehyde production using cadmium sulfide nanorods decorated with small cobalt nanoparticles under visible light. *J Catal* **357**, 147-153 (2018).
 31. Xing F, Zeng R, Cheng C, Liu Q, Huang C. POM-incorporated ZnIn₂S₄ Z-scheme dual-functional photocatalysts for cooperative benzyl alcohol oxidation and H₂ evolution in aqueous solution. *Appl. Catal. B* **306**, 121087 (2022).
 32. Wan J, *et al.* Exploring the Polarization Photocatalysis of ZnIn₂S₄ Material toward Hydrogen Evolution by Integrating Cascade Electric Fields with Hole Transfer Vehicle. *Adv. Funct. Mater.* **32**, 2203252 (2022).

33. Tayyab M, *et al.* Simultaneous hydrogen production with the selective oxidation of benzyl alcohol to benzaldehyde by a noble-metal-free photocatalyst VC/CdS nanowires. *Chinese J. Catal.* **43**, 1165-1175 (2022).
34. Kasap H, *et al.* Solar-Driven Reduction of Aqueous Protons Coupled to Selective Alcohol Oxidation with a Carbon Nitride–Molecular Ni Catalyst System. *J. Am. Chem. Soc.* **138**, 9183-9192 (2016).
35. Kasap H, *et al.* Interfacial Engineering of a Carbon Nitride–Graphene Oxide–Molecular Ni Catalyst Hybrid for Enhanced Photocatalytic Activity. *ACS Catal.* **8**, 6914-6926 (2018).
36. Zhang L, Jiang D, Irfan RM, Tang S, Chen X, Du P. Highly efficient and selective photocatalytic dehydrogenation of benzyl alcohol for simultaneous hydrogen and benzaldehyde production over Ni-decorated Zn_{0.5}Cd_{0.5}S solid solution. *J. Energy Chem.* **30**, 71-77 (2019).
37. Lin F, *et al.* Electrostatic self-assembly combined with microwave hydrothermal strategy: construction of 1D/1D carbon nanofibers/crystalline g-C₃N₄ heterojunction for boosting photocatalytic hydrogen production. *Nano Energy* **99**, 107432 (2022).
38. Meng X, Zhang C, Dong C, Sun W, Ji D, Ding Y. Carbon quantum dots assisted strategy to synthesize Co@NC for boosting photocatalytic hydrogen evolution performance of CdS. *Chem. Eng. J.* **389**, 124432 (2020).
39. Qin J, Zeng H. Photocatalysts fabricated by depositing plasmonic Ag nanoparticles on carbon quantum dots/graphitic carbon nitride for broad

- spectrum photocatalytic hydrogen generation. *Appl. Catal. B* **209**, 161-173 (2017).
40. Liu Y, *et al.* In-situ construction of hierarchical CdS/MoS₂ microboxes for enhanced visible-light photocatalytic H₂ production. *Chem. Eng. J.* **339**, 117-124 (2018).
 41. Chen W, Yan R-Q, Zhu J-Q, Huang G-B, Chen Z. Highly efficient visible-light-driven photocatalytic hydrogen evolution by all-solid-state Z-scheme CdS/QDs/ZnIn₂S₄ architectures with MoS₂ quantum dots as solid-state electron mediator. *Appl. Surf. Sci.* **504**, 144406 (2020).
 42. Wei R-B, *et al.* Dual-cocatalysts decorated rimous CdS spheres advancing highly-efficient visible-light photocatalytic hydrogen production. *Appl. Catal. B* **231**, 101-107 (2018).
 43. Jana B, Reva Y, Scharl T, Strauss V, Cadranal A, Guldi DM. Carbon Nanodots for All-in-One Photocatalytic Hydrogen Generation. *J. Am. Chem. Soc.* **143**, 20122-20132 (2021).
 44. Zhang D, *et al.* 0D/2D Z-scheme heterojunctions of Zn-AgIn₅S₈ QDs/ α -Fe₂O₃ nanosheets for efficient visible-light-driven hydrogen production. *Chem. Eng. J.* **417**, 128275 (2020).
 45. Hu X, Zhan Z, Zhang J, Hussain I, Tan B. Immobilized covalent triazine frameworks films as effective photocatalysts for hydrogen evolution reaction. *Nat. Commun.* **12**, 6596 (2021).
 46. Dharmi BS, Tripathi RPN, Hoxie DJ, Appavoo K. Revealing Ultrafast Carrier

- Dynamics of Hybrid Perovskites at Various Stages of Nucleation and Growth Kinetics. *Adv. Opt. Mater.* **11**, 2201832 (2023).
47. Berberan-Santos MN, Bodunov EN, Valeur B. Mathematical functions for the analysis of luminescence decays with underlying distributions 1. Kohlrausch decay function (stretched exponential). *Chem. Phys.* **315**, 171-182 (2005).
48. AC/DC Module User's Guide, pp. 75-84. COMSOL Multiphysics COMSOL AB, Stockholm, Sweden. (2021).
49. Cussler EL. Diffusion: mass transfer in fluid systems, third ed. *Cambridge University Press*, (2009).
50. Li XY, *et al.* Mechanism of Cations Suppressing Proton Diffusion Kinetics for Electrocatalysis. *Angew. Chem. Int. Ed.* **62**, e202218669 (2023).